Review on sorption materials and technologies for heat pumps and thermal energy storage

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Abstract

Sorption is used for absorption/adsorption heat pumps (sorption refrigeration) and sorption for thermal energy storage (TES). This paper is the first review where the research on both applications is shown together. Sorption has advanced very much due to the immense amount of research carried out around heat pumping and solar refrigeration. Moreover, sorption and thermochemical heat storage attracted considerable attention recently since this technology offers various opportunities in the design of renewable and sustainable energy systems. The paper presents the operation principle of the technology and the materials used or in research are listed and compared. Absorption heat pumping and refrigeration research is today more focussed in the decrease of unit costs and increase of energy efficiency, adsorption is focussed in finding more efficient working pairs, and storage is testing the first prototypes and designing new ones with different or enhanced storage materials and new reactor concepts to optimize energy output.

Keywords: sorption; absorption; adsorption; materials; technologies; heat pumps; thermal energy storage

Nomenclature

COP: Coefficient of Performance

SCP: specific cooling power

TES: Thermal energy storage

Qchar: heat of charging

Qsens: sensible heat

Qcond: heat of condensation

Qbind: heat of binding

HX: heat exchanger

SHX: solution heat exchanger

PTX: Pressure-Temperature concentrationPCPs: porous coordination polymers

MOFS: metal organic frameworks

TCM: Thermochemical material

DHW: domestic hot water

HTDU: high-temperature discharging unit

LTDU: low-temperature discharging unit

T: temperature [^{o}C]

AlPOs: aluminophosphates

SAPOs: silico-aluminophosphates

Subscripts

h : heat

Greek letters

1. Introduction

Sorption is a technology used for absorption/adsorption heat pumps (sorption refrigeration) and sorption for thermal energy storage (TES). *Although both technologies for heat pumps and sorption for TES use the same or very similar materials and technologies, they have been rarely considered together to learn from one to the other. This review aims on contributing on this collaborative learning by presenting for the first time the materials and technologies used in sorption systems for cooling, heat pumping and storage.*

The existing systems for producing cold, especially when using solar thermal energy, are based mainly on the phenomena of sorption: the process by absorption liquid-gas and the process by adsorption solid-gas [1-3]. The adsorption process concerns separation of a substance from one phase, accompanied by its accumulation or concentration on the surface of another. On the other hand, absorption is the process in which material transferred from one phase to another, (e.g. liquid) interpenetrates the second phase to form a solution. In general, the main differences between absorption and adsorption are located in the nature of the sorbent and the duration of the sorption cycle, which is significantly longer for adsorption [4]; therefore the main difference is that in absorption the sorbent is a pumplable fluid, therefore the heat is recovered easier but movable parts can be a disadvantage. This kind of cold storage system, which can be driven by electricity, industry waste heat, or solar energy, contributes significantly to the concept of sustainable system development.

The key figure describing the efficiency of a sorption refrigeration system is the thermal coefficient of performance ($COP_{thermal}$), which is defined as follows [4,5]:

$$COP_{thermal} = \frac{\text{cooling power}}{\text{energy received by system}} \qquad \text{Eq. 1}$$

For sorption thermal storage systems, the energy for charging includes sensible heat, a prerequisite energy to heat up the reactor to a required desorption temperature, and the heat of desorption, which includes the heat of condensation and the heat of binding [6]:

$$Q_{char} = Q_{sens} + Q_{des} \qquad \text{Eq. 2}$$

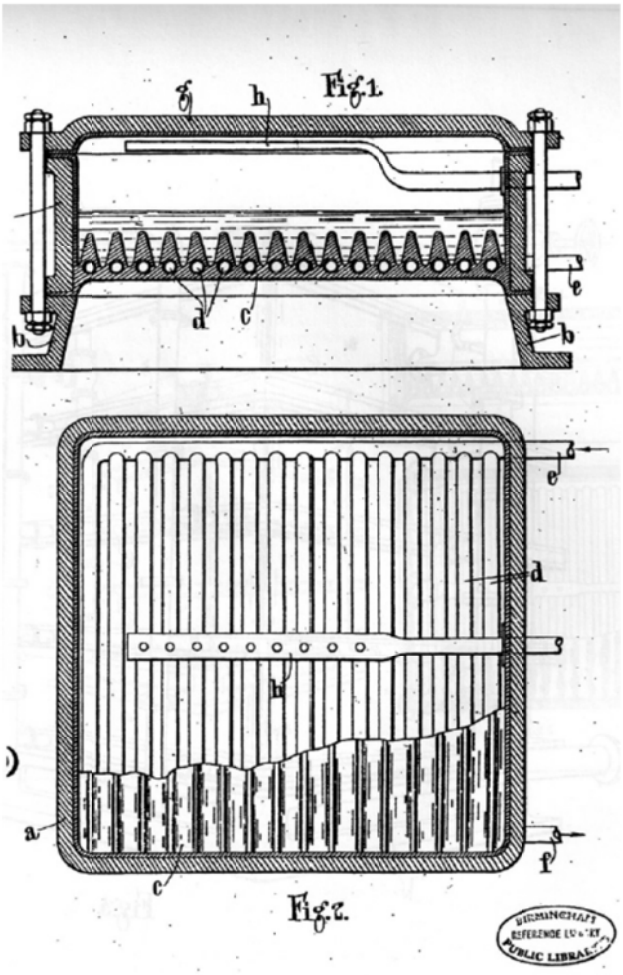
$$Q_{des} = Q_{cond} + Q_{bind} \qquad \text{Eq. 3}$$

For cold storage, the value of Qcond/Qchar almost equals the cooling coefficient of performance (COPc) [6].

2. Sorption heat pump and cooling

2.1. Technologies

Adsorption cycles for heat pumping or cooling/refrigeration might seem like a relatively new, but the history of solid sorption systems is long dating from Faraday (1823) [7-9]. Patents on refrigeration machines started in early 1900s, being the first one that from Dunsford (1915) for ammonium nitrate as adsorbent for marine applications (Figure 1) [10]. The technology restarted to rise interest again in the early 1970s, with pioneer work by Alefeld (1975) [11] and Tchernev (1977) [12]. In the late 1980s and 1990s there was an explosion of activity worldwide, with conferences, published papers and the first products appearing in the market. Very recently the environmental and energy cost concerns have led to new research and development of small scale products for air conditioning, solar air conditioning, and heat pumping. Interest in storage is the most recent studied application.



105
106 **Figure 1. Dunsford's generator of 1915 [7,10]**
107

115 Sorption systems are either open or closed cycles [2-5,13-16]. Open cycles are mainly desiccant
116 systems, while closed cycles are adsorption or absorption systems. The main differences
117 between adsorption and absorption are located in the nature of the sorbent and the duration of
118 the sorption cycle. The general operating principal of solar closed cycle sorption refrigerator is
119 presented in Figure 2. The process of adsorption concerns separation of a substance from one
120 phase and its concentration on the surface of another. Adsorption systems are based on a
121 physical or chemical reaction process in which the molecules of one substance are adsorbed on
122 the internal surface of another substance [4,17].
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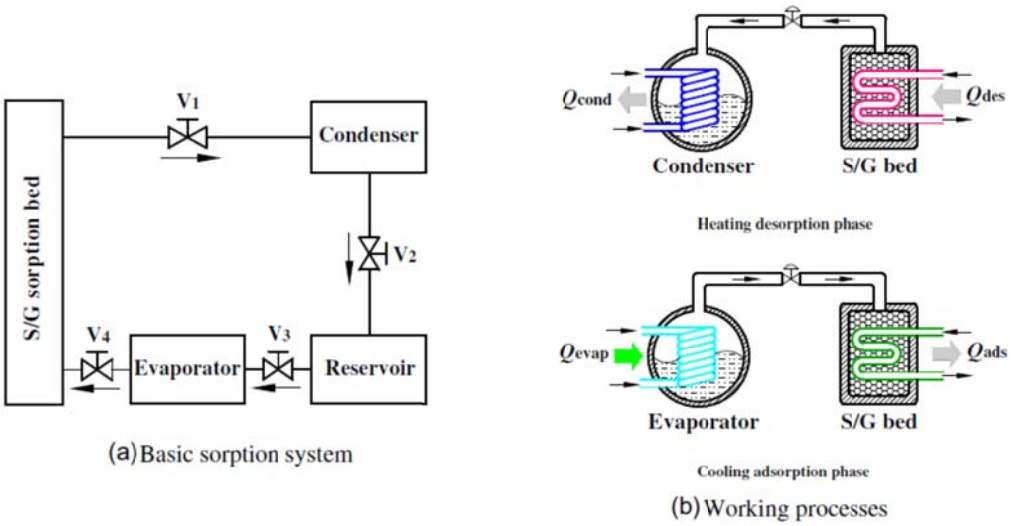


117 **Figure 2. Schematic diagram of a basic solid-gas sorption refrigeration cycle [18].**

118

124 Absorption systems are the oldest and most common heat driven refrigeration systems
125 [4,16,19,20]. On the low-pressure side, an evaporative refrigerant is absorbed by the absorbent
126 formulating a weak absorbent solution. The weak solution is directed to the generator where the
127 pressurisation takes place by desorption of the refrigerant. The refrigerant then undergoes a
128 common cooling cycle, while the weak solution is directed to the absorber and the cycle is
129 repeated.

125

129 Ziegler [13] carried out a comparison between liquid (absorption) and solid (adsorption)
130 sorption (Figure 3), claiming that sorption chillers can be operated with low driving
131 temperature, but the specific costs will be high and the COP will be low. Such comparison is
132 done based on the characteristic temperature difference, ΔΔT, defined as:

130

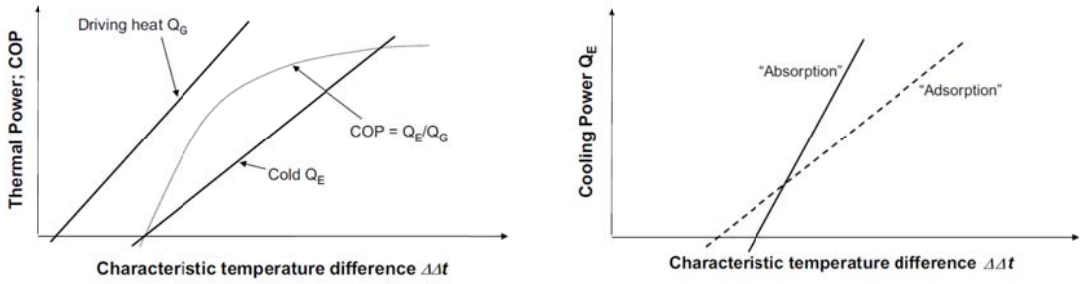
131 $$\Delta\Delta T = (t_G - t_A) - (t_C - t_E) \cdot B \qquad \text{Eq. 4}$$

134 where t_G is the temperature of the generator (desorber), t_A is the temperature of the absorber, t_C
135 is the temperature of the condenser, t_E is the temperature of the evaporator, and B is the Düring
136 coefficient.

135

137 Demir at al. [21] and Sarbu and Sebarcievici [5] compared the different characteristics of both
138 systems (Table 1).

138

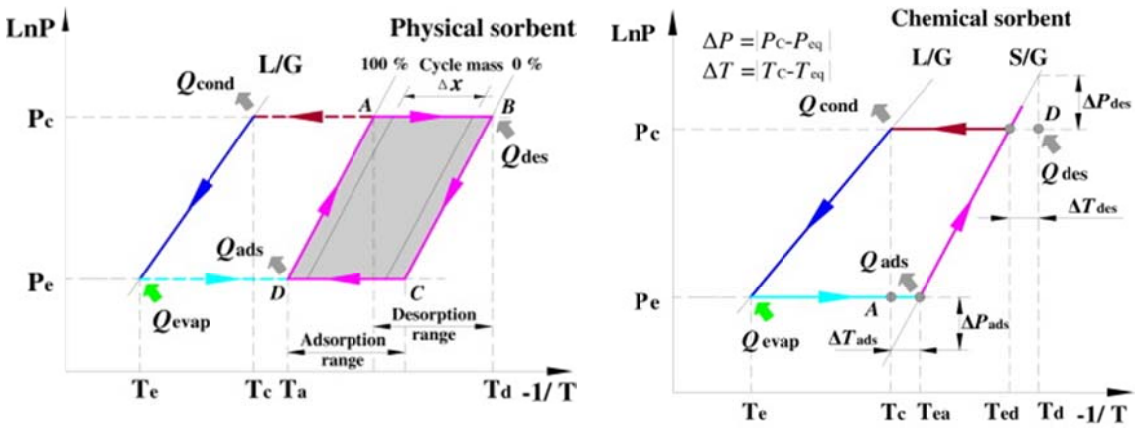


140 **Figure 3. Thermal power (COP) and cooling power comparison between absorption and adsorption cycles**
141 **[13].**
141
142 **Table 1. Comparison between absorption and adsorption systems [5,21].**

Types of heat pumps	Working pairs	Coefficient of performance
Adsorption	Carbon/methanol	0.12-1.06
	Zeolite/water	0.28-1.4
	Silica gel/water	0.25-0.65
Absorption	Methanol/water	0.7-1.1
	Lithium bromide/water	
Vapour compression		3-4

143

149 The sorption refrigerator includes one or several reactors, i.e. regenerator(s), absorber(s),
150 adsorber(s), generator(s) etc., depending on the specific cycle and the sorption pair, and of
151 course the condenser and the evaporator, which exchange refrigerant vapour with the thermal
152 compressor. The working principle of solid physisorption is based on the Van der Waals force
153 between a sorbent and a refrigerant gas. The basic adsorption cycle for cooling consists of four
154 processes represented in Figure 4 [20,22-26].



151 **Figure 4.(a) Working principle of the physiosorption (adsorption) refrigeration cycle; (b) Working principle of**
152 **thermochemical sorption (absorption) refrigeration cycle [22].**

158 The working principle of solid thermochemical sorption refrigeration cycle is shown in Figure
159 4b [22]. The working pressure and temperature are the functional equation of one variable, and
160 the working region between the sorbent and the refrigerant is the solid-gas equilibrium line.
161 Thus, once the operating temperature/pressure is away from the solid-gas equilibrium
162 temperature/pressure, chemical reaction would occur between the sorbent and the refrigerant.
163 The driving equilibrium drop is the only contributor to the chemical reaction in solid-gas
164 thermochemical sorption refrigeration system.
159
172 In principle, a sorption cycle is a four temperature cycle, but the two heat quantities Q_{SO} and
173 Q_{CO}, commonly rejected to the intermediate temperatures T_{SO} and T_{CO} respectively, are
174 transferred to the same heat sink. In technical terms, the heat is removed from a cold water
175 stream in a closed loop, passing serially from the generator, the condenser and the cooling
176 tower. Thus, it is assumed that $T_{SO} = T_{CO}$ and the cycle is considered to be a three temperature
177 cycle. The heat Q_{GE} is supplied by the heat source (solar collectors) at temperature T_{GE} to the
178 thermal compressor (sorption system), where it induces desorption of the refrigerant vapour at
179 the condenser pressure. The vapour is liquefied in the condenser at the intermediate temperature
180 T_{CO}. When the sorption system is cooled down back to the intermediate temperature T_{SO}, it
181 reabsorbs vapour, which is produced by the vaporisation of the liquefied refrigerant in the
182 evaporator. The vaporisation heat Q_{EV} derives from the cooling space, through the chilled water
183 circulation. The coefficient of performance of a sorption refrigerator is expressed as the amount
184 of cooling delivered (cold produced) divided by the amount of the required heat input:
173

$$\mathrm{COP} = \frac{Q_{\mathrm{EV}}}{Q_{\mathrm{GE}}} \qquad \text{Eq. 5}$$

174
175
177 where, Q_{EV} denotes the heat removed from the cooled space; and Q_{GE} denotes the heat derived
178 from the heat source to the generator (desorber).
178
186 Based on the thermodynamic cycle of operation principle, absorption cycles are considered
187 single-effect, half-effect, double-effect, and triple-effect [16,19]. Table 2 shows a comparison
188 on the performance of different absorption cooling systems [5,14,26]. The single-effect system
189 is the simplest type and the most used in commercial devices [27,28].The half-effect cycle, also
190 called two-stage or double-lift cycle, can provide cold with a relatively low driving temperature.
191 The COP of this cycle is roughly half of the single-effect cycle and so often called half-effect.
192 Single-effect absorption cooling system is based on the basic absorption cycle that contains a
193 single absorber and generator as shown in Figure 5. In the generator G, the refrigerant is

separated from the absorbent by the heat provided by the solar collector. The vapour-refrigerant are condensed in condenser C, then laminated in expansion valve EV1 and evaporated at low pressure and temperature in the evaporator V. The cooled refrigerant is absorbed in the absorber Ab by weak-solution that returns from generator after the lamination in the expansion valve EV2. The rich-mixture created in absorber is pumped by pump P and returned in G. The usual a solution heat exchanger (SHX) can be used to improve cycle efficiency [16]. A 60% higher COP can be achieved by using the SHX [29]. The absorption being exothermic, the absorber is chilled with cooling water. The half-effect absorption refrigeration cycle has discussed by Arivazhagan et al. [30] and Gebreslassie et al. [31].

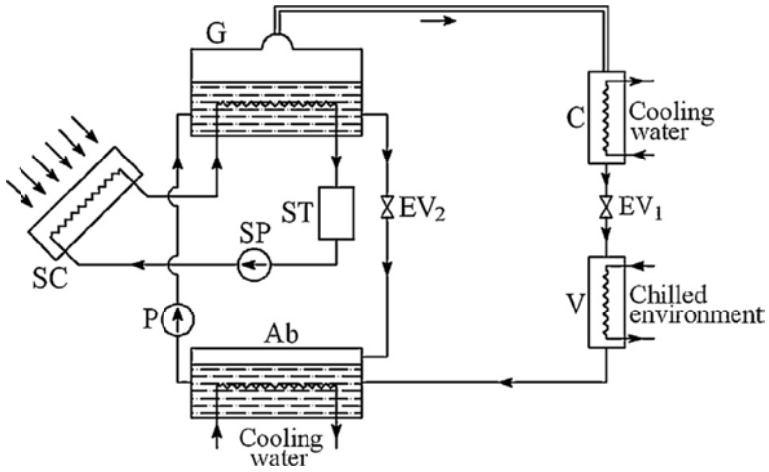


Figure 5. Schematic of solar absorption cooling systems [5,14].

Double-effect systems can be achieved by adding an extra stage as a topping cycle on the single-effect cycle. They have a double COP value compared with that of single-effect systems, nearly 1.2. However, their working liquids must achieve higher temperature, more than 130 ºC. Double-effect absorption cooling technology was launched in 1956 for developing the system performance within a heat source at higher temperature [32]. Figure 6 illustrates a double-effect absorption system with a H_2O/LiBr pair. The cycle begins with generator G-I providing heat to generator G-II. The condenser C rejects the heat and passes the working fluid towards the evaporator V; within this step, the required refrigeration occurs. Then, the fluids pass through the heat exchangers HX-I and HX-II from the absorber Ab to G-I by means of a pump P. Through this process, HX-II can pass the fluids to G-II and then G-II passes to HX-I. The complete cycle follows three different pressure levels: high, medium and low. Many researchers have studied and analysed the double-effect absorption cooling machines [33,37].

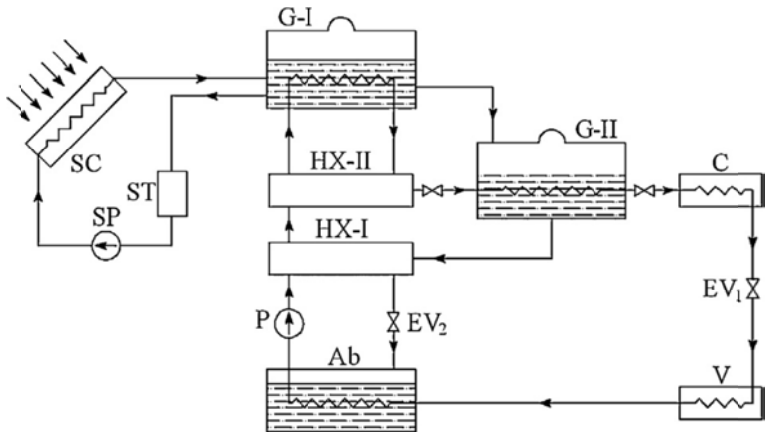


Figure 6. Schematic of solar assisted double-effect H_2O/LiBr absorption system [5,14].

Triple-effect absorption cooling can be classified as single-loop or dual-loop cycles [5,14]. Single-loop triple-effect cycles are basically double-effect cycles with an additional generator and condenser. The resulting system with three generators and three condensers operates similarly to the double-effect system. Primary heat concentrates absorbent solution in a first-stage generator at about 200–23 ºC. A fluid pair other than H_2O/LiBr must be used for the high temperature cycle. The refrigerant vapour produced is then used to concentrate additional absorbent solution in a second-stage generator at about 150 ºC. Finally, the refrigerant vapour produced in the second-stage generator concentrates additional absorbent solution in a third-stage generator at about 93 ºC. The usual solution heat exchangers can be used to improve cycle efficiency. Theoretically, these triple-effect cycles can obtain COPs of about 1.7 [38].

Table 2. Characteristics of absorption cycles.

Absorption cooling	T_{evap} (ºC)	T_{ref} (ºC)	T_{gen} (ºC)	$T_{heating}$ (ºC)	x_{weak} (kg/kg)	x_{strong} (kg/kg)	COP_{Carnot}	α	COP	EER (Bry/Wh)	General remarks of the technology
Half-effect H_2O-LiBr	2 [26]	30 [26]	57 [26]	67 [26]	0.560 [26]	0.472 [26]	0.80 [26]	0.44 [26]	0.35 [26]	---	Within the optimum temperature range of 65-70 ºC, the COP is 0.36 and the evaporation temperature is -7 ºC [5,30]
		40 [26]	78 [26]	88 [26]	0.515 [26]	0.418 [26]	0.78 [26]	0.44 [26]	0.34 [26]	---	The pair is able to provide the same COP as a conventional cooling system [5,39]
		50 [26]	98 [26]	108 [26]	0.470 [26]	0.364 [26]	0.74 [26]	0.44 [26]	0.33 [26]	---	The system has 22% lower exergetic efficiency compared to the single-effect system [5,40]
Single-effect H_2O-LiBr	2 [26]	30 [26]	82 [26]	92 [26]	0.440 [26]	0.328 [26]	1.44 [26]	0.50 [26]	0.72 [26]	---	---
		---	---	86.5 [5,14,42]	---	---	---	---	0.7 [5,14,42]	2.39 [5,14, 26,42]	A COP approximately 60% higher can be achieved by using a vacuum tubular collector [5,43]
		40 [26]	94 [26]	104 [26]	0.360 [26]	0.328 [26]	1.06 [26]	0.50 [26]	0.53 [26]	---	A system capacity of 70 kW can be achieved by using a vacuum tubular collector (108 m^2) with flat plate collectors 9124 m^2 [5,28]
		50 [26]	---	---	---	---	---	---	---	---	COP is increased by 15% using a portioned hot water tank with a flat plate collector [5,27]
		---	---	80-100 [19]	---	---	---	0.5-0.7 [19]	---	---	Simplest and widely used [19]
		---	---	---	---	---	---	---	---	---	Water cooled absorber is required to prevent crystallization at higher concentration [19]
Single-effect NH_3- H_2O	2 [26]	30 [26]	76 [26]	86 [26]	0.550 [26]	0.460 [26]	1.29 [26]	0.46 [26]	0.60 [26]	---	Rectification of refrigerant is required [19]
		40 [26]	108 [26]	118 [26]	0.475 [26]	0.370 [26]	1.29 [26]	0.46 [26]	0.59 [26]	---	Working solution is environmental friendly [19]
		50 [26]	130 [26]	140 [26]	0.425 [26]	0.310 [26]	1.14 [26]	0.46 [26]	0.52 [26]	---	No crystallization problem [19]
		---	---	120-150 [19]	---	---	---	---	0.5 [19]	---	Suitable for using as heat pump due to with operation range [19]
Double-effect H_2O -LiBr	2	30 [26]	132 [26]	142 [26]	0.440 [26]	0.328 [26]	2.47 [26]	0.52 [26]	1.29 [26]	---	The double-effect chillers with through collectors show the maximum potential savings [5,44]
		---	---	130 [5,14,42]	---	---	---	---	1.2 [5,14,42]	4.10 [5,14,42]	The system has almost double (0.96) the COP compared to the single-effect system [5,19]
		40 [26]	166 [26]	176 [26]	0.385 [26]	0.300 [26]	2.08 [26]	0.52 [26]	1.08 [26]	---	High performance cycle available commercially [19]

		50 [26]	---	---	---	---	---	---	---	---	Heat of condensation from the first effect is used as heat input for the second stage [19]
		---	---	120-150 [19]	---	---	---	---	0.8-1.2 [19]	--	---
Triple-effect	---	---	---	220 [5,14,42]	---	---	---	---	1.7 [5,14,42]	5.80 [5,14,42]	High complexity of the control system [19]
		---	---	200-230 [19]	---	---	---	---	1.4-1.5 [19]	---	Likely to be direct fired as the input temperature is quite high [19]
		---	---	---	---	---	---	---	---	---	Requires more maintenance as a result of high corrosion due to the operating temperature [19]
Hybrid	---	---	---	---	---	---	---	---	---	---	The types of systems are widely implemented for the cooling in larger places [5,45]

Infante Ferreira and Kim [26] carried out a techno-economic comparison of the different solar cooling technologies, including absorption and adsorption systems. Table 3 gives an estimation of the investment costs, including installation costs, of the several cooling cycle technologies. For comparison purposes, it also shows values proposed in recent publications. Some systems require an engine (Stirling or Rankine). A value of 1700 €/kW shaft power was considered.

Table 3. Specific prices of different cooling cycles (thousands €/kW).

Vapour compression	Half-effect absorption	Single-effect absorption	Double-effect absorption	Adsorption	Desiccant	Reference
300	---	400	---	850	---	[26,46]
200	---	400	300	500	---	[25,26]
210	---	250	550	---	---	[26,47]
---	---	---	---	---	370	[26,48]
---	---	210	855	855	1065	[26,49]
300	---	400	700	600	---	[26,50]
250	700	400	700	700	700	[26]

As example, the main features of the possible solar refrigeration technologies, with respect to their COP, application and input temperature needed are presented in Table 4 [4].

Table 4. Main features of solar sorption refrigeration technologies [4].

	Absorption				**Adsorption**		
	LiBr/water		**Water/NH_3**		**One-stage (silica gel/water)**	**Two-stage (silica gel/water)**	**Adsorber /collector**
	Single-effect	**Double-effect**	**Single-stage**	**Two-stage**			
COP	0.5-0.75	0.8-1.2	0.5	1.2-1.3	0.3-0.7	0.35	0.1-0.5
Application	Air-conditioning	Air-conditioning	Air-conditioning Refrigeration	Air-conditioning Refrigeration	Air-conditioning	Air-conditioning	Refrigeration
Input temperature (ºC)	80-100	100-160	120-150		60-90	50-75	

2.2. Materials

2.2.1. Absorption systems

There are two main absorption systems: lithium bromide/water and water-ammonia [1-4,14,16,52 -54]. A comparison between both systems is presented in Table 5. Broadly speaking, NH_3–H_2O systems are often used for refrigeration and in industrial applications while H_2O–LiBr systems are more suitable for air-conditioning purposes.

Table 5.Comparison between the absorption systems with NH_3-H_2O and H_2O-LiBr [1,5]

	Water/NH_3	Li/water
Advantages	Evaporative at the temperature below 0ºC	High COP Low operation pressures Environmental friendly and innoxious Large latent heat of vaporization
Disadvantages	Toxic and dangerous for health In need of a column of rectifier Operation at high pressure	The risk of congelation Relatively expensive (LiBr)

The basic lithium bromide–water (LiBr) absorption cycle has been in use in refrigeration applications since the 1940s. Its key characteristics are determined by the pressure–temperature concentration (PTX) equilibrium chart, the solution cycles, the individual components and the chemical additives. Its functional performance is mainly characterised by the partial load operation and the particularities of maintenance of the system. In this cycle, LiBr is the absorbent and water is the refrigerant. The output of a LiBr system can be as low as 4 ºC. These absorption systems are categorised by the number of times the solution is heated to produce refrigerant vapours, referred to as the number of effects. Figure 7 shows a typical single-effect solar driven LiBr–water absorption refrigeration system.

The second widely used refrigeration system is based on the water–ammonia absorption cycle. This system is mainly encountered in industrial applications, in chemical processes, in the food industry and in drying processes. It is also suitable for solar energy applications. In the case of a water–ammonia absorption cycle, water is the absorbent and ammonia is the refrigerant (i.e. the opposite of the LiBr cycle). The cooling output in most cases is liquid ammonia, separated from the ammonia in the water–ammonia absorption cycle machine, as opposed to the chilled water used in LiBr absorption systems. Due to the fact that ammonia is the refrigerant, the output of a water–ammonia absorption cycle system can be as low as -60 ºC. If the system is installed in a closed space, ventilation is required by the standards for ammonia refrigeration. Water–ammonia absorption cycle systems are categorised according to the number of evaporator

stages. A single-stage system has one stage of evaporation/absorption, and a two-stage system has two stages of evaporation/absorption. The number of stages of evaporation can be increased in order to reach the cooling and the refrigeration temperature required by the design parameters. Water–ammonia absorption cycle systems are tailor-made systems for each application. The operational principles of a water–ammonia absorption cycle system are similar to those of LiBr absorption machines.

On the other hand, Du et al. [51] proposed an air-cooled two-stage NH_3-H_2O absorption refrigeration system is proposed for potential application of residential small scale cooling system driven by solar heated hot water. The study reveals the technical feasibility of the air-cooled two-stage NH3-H2O absorption system and provides an alternative low-cost small bulk solar absorption air-conditioning.

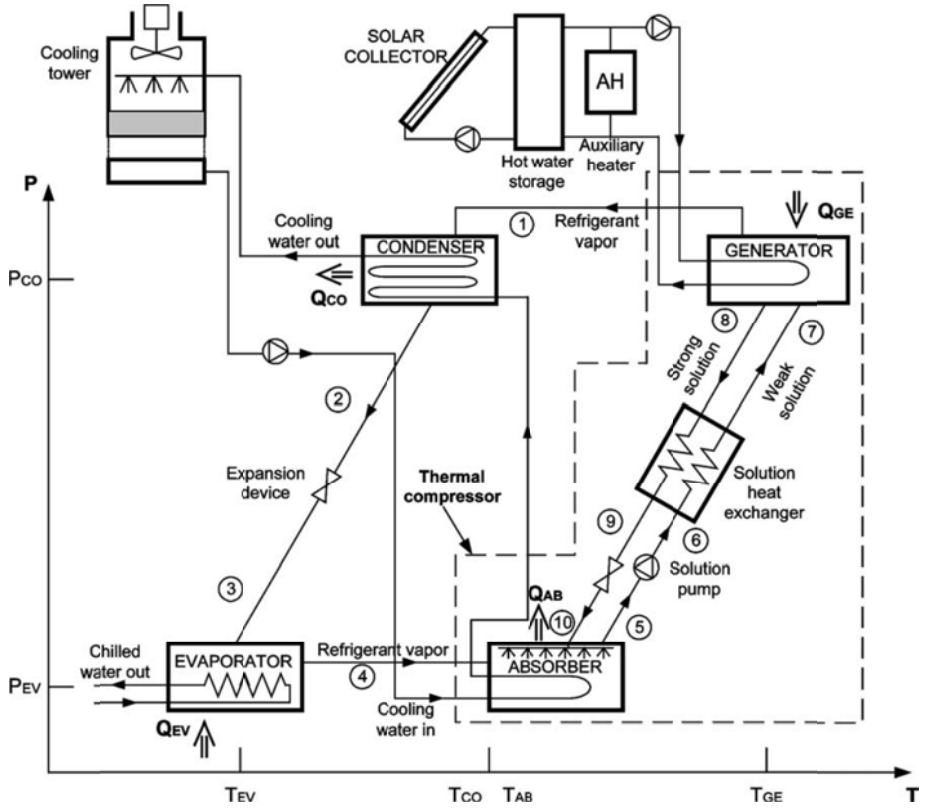


Figure 7. Schematic of a solar driven LiBr-water single-effect absorption refrigeration System [4].

Table 6. Overview of solar absorption refrigeration studies with LiBr/H_2O and NH_3/H_2O

Technology	Application	Q_e[kW]	A_s[m^2]	Efficiency - $\eta_{heat-cool}$	COP	Reference
Single-effect LiBr/H2O	Space cooling/ heating	---	---	---	---	[16,25,58-64]
	Space cooling	4	36	0.11	---	[25,65]
		210	1577	0.31	---	[25,66]
		90	316	0.26-0.36	---	[25,67]
		35	49.9	0.34	---	[25,68]
		---	---	---	0.490	[5,69]
		---	---	---	0.620	[5,70]
		---	---	---	0.660	[5,71]
		---	---	---	0.740	[5,72]
	Prototype chiller	10	---	0.37	---	[25,73,74]
		16	---	0.40	---	[25,75]
Double-effect LiBr/H2O	Fuel-fired-solar-assisted prototype	---	---	---	---	[25,76,77]
	Cooling/steam generation	140	180	0.5-0.6	---	[25,78]
NH3/H2O	Diffusion/absorption prototype	<2.5	---	0.1-0.25	---	[25,79-81]
	Refrigeration/ heat pump	---	---	---	---	[16,25,79,82-88]
	Wine cooling	10	100	---	---	[5,89]
	Space cooling	15	---	0.27	---	[5,90]
		---	---	---	0.427	[5,91]
		---	---	---	0.550	[5,92]

Table 7. Other working pairs for absorption

Working pair	COP	Comments	Reference
$NH3/CaCl_2$	0.10	Ice production 6 kg/m2 of collector area	[1,16,93]
$NH3/SrCl_2$	---	---	[1,93]
	0.049 (1994) 0.045-0.082 (1995)	---	[1,16,94]
NH3/IMPEX (80% $SrCl_2$+20% graphite	0.143	1.45 kWh/day	[1,16,95]
Organic fluid mixtures trifluoroethanol (TFE)–tetraethylenglycol dimethylether (TEGDME or E181) and methanol–TEGDME	15% higher than NH3-H_2O	Simulations	[1,16,96,97]
Aqueous ternary hydroxide 40:36:24 (NaOH:KOH:CsOH)	Higher than NH3-H2O	Operates at broader temperatures than NH3-H_2O	[1,16,98]
NH3/LiNO3 mixture	0.15-0.4	Produce 11.8 kg of ice	[1,16,99]
NH3/Water-NaOH mixture	---	---	[16,100]
$_{H2O}$/Ionic liquid (1-ethyl-3-methilimidazolium dimethylphosphate [EMIM][DMP])	---	---	[16,101,102]
H2O/Ionic liquid (1-ethyl-3-methylimidazolium ethylsulfate [EMISE])	---	---	[16,103]
H2O/Ethyleneglycol	---	---	[16,104]
H2O/Monomethylamine	---	---	[16,105]

2.2.2. Adsorption systems

In principle there are two broad categories of adsorption systems: continuous and intermittent, with intermittent systems being more suitable for the utilisation of solar energy since they are daily cycle systems [2,4,56]. Another structural categorisation of adsorption systems concerns the nature of the adsorption effect and particularly whether or not it is a physical phenomenon or whether or not it includes a chemical reaction [4,22,106-111]. When fixed adsorbent beds are employed, which is the common practice, these cycles can be operational without moving parts other than magnetic valves. This results in low vibration, mechanical simplicity, high reliability and a very long lifetime. The use of fixed beds also results in intermittent cycle operation, with adsorbent beds changing between adsorption and desorption stages. Hence, when constant flow of vapour from the evaporator is required in order to provide continuous cooling, two or more adsorbent beds must be operated out of phase [112]. Compared to absorption, adsorption chillers are more expensive and their commercial availability is still limited. Their COP is lower than that of the absorption chillers, but they can utilise heat at lower temperature, they can thus be driven by flat plate solar collectors more efficiently. Figure 8 shows a single-stage silica gel/water adsorption chiller driven by solar energy.

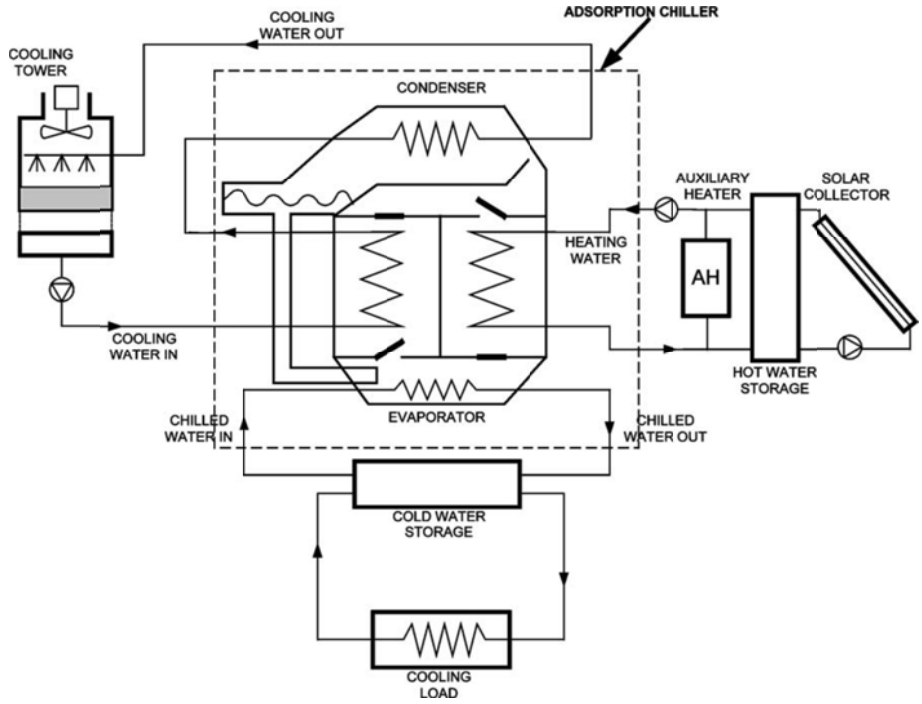


Figure 8. Schematic of a single-stage silica gel/water adsorption chiller [4].

In addition, Pan et al. [113] developed a silica gel-water adsorption chiller driven by low-grade heat. This chiller was tested under different conditions and it features the periodic variations of

temperatures and cooling power and the obtained cooling power, COP and SCP are 42.8 kW, 0.51 and 125.0 W/kg, respectively which were in range with those described in the literature.

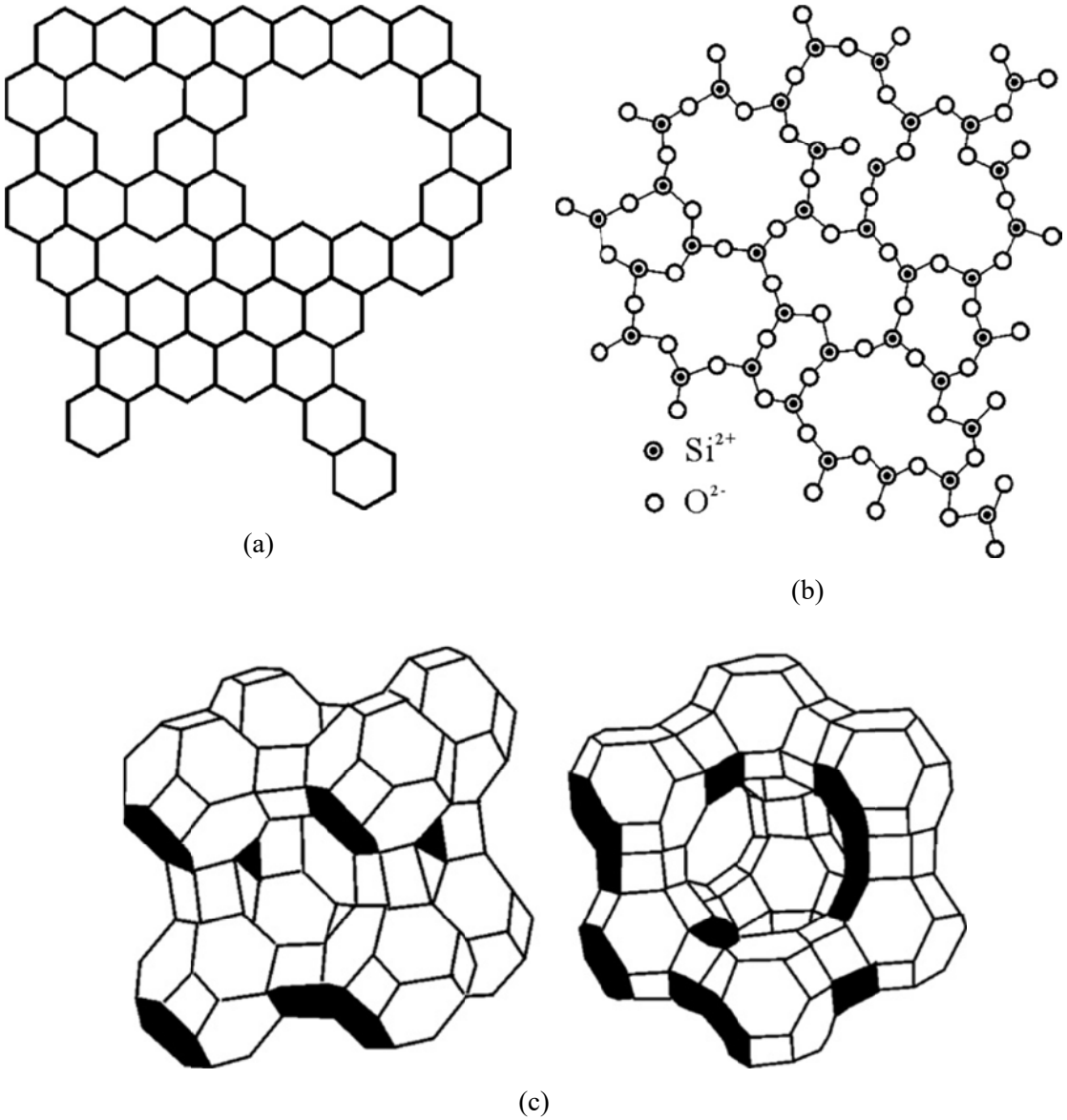
Physical adsorption is caused by van de Walls force between the molecules of the adsorbent and the adsorbate [22,114]. Physical adsorbents with mesopores can adsorb consecutives layers of adsorbate, while those with micropores have the volume of the pores filled with the adsorbate. Physical adsorbents develop the selectivity to the adsorbate after the former undergo specific treatments, like react under a gas stream or with certain agents. The kind of treatment will depend on the type of sorbents [115]. Chemical adsorption is caused by the reaction between adsorbates and the surface molecules of adsorbents. Electron transfer, atom rearrangement and fracture or formation of chemical bond always occurs in the process of chemical adsorption [116]. Only one layer of adsorbate reacts with the surface molecules of chemical adsorbent. The adsorbate and adsorbent molecules after adsorption never keep their original state, e.g., complexation occurs between chlorides and ammonia. Moreover, there are the phenomena of salt swelling and agglomeration, which are critical to heat and mass transfer performance.

Composite adsorbents [117-119] started to be studied about in the late 80s [120], and they aimed to improve the heat and mass transfer performance of the original chemical adsorbents [118,121,122]. This kind of adsorbent is usually obtained by the combination of a chemical adsorbent and a porous medium, that can be or not a physical adsorbent, such as activated carbon, graphite, carbon fibre, etc. [118,123,124].

Physical adsorbents used are activated carbon, activated carbon fibre, silica gel, and zeolite [22]. The activated carbon is made of materials such as wood, peat, coal, fossil oil, chark, bone, coconut shell and nut stone. The structure of activated carbon is shown in Figure 9a. The microcrystal for the activated carbon produced from bone is a six element carboatomic ring [115], and the adsorption performance is influenced by the functional groups that are connected to the carboatomic ring. The silica gel is a type of amorphous synthetic silica. It is a rigid, continuous net of colloidal silica (Figure 9b), connected to very small grains of hydrated SiO_4 [125]. The hydroxyl in the structure is the adsorption centre because it is polar and can form hydrogen bonds with polar oxides, such as water and alcohol. The adsorption ability of silica gel increases when the polarity increases. One hydroxyl can adsorb one molecule of water. Zeolite is a type of aluminasilicate crystal composed of alkali or alkali soil. The chemical formula of zeolite is:

$$M_{y/n}[(AlO_2)_y(SiO_2)_m]zH_2O \quad \text{Eq. 6}$$

where y and m are all integers and m/y is equal or larger than 1; n is the chemical valence of positive ion of M; and z is the number of water molecule inside a crystal cell unit. A crystal cell unit of zeolite is shown in Figure 9c. The positive ion must have its electric charge balanced with the electric charge of aluminium atom. The net electric charge of each aluminium atom is -1. Water can be removed by heating. There are about 40 types of natural zeolites, and the main types for adsorption refrigeration are chabazite, sodium chabazite, cowlesite and faujasite. About 150 types of zeolitescan be artificially synthesized, and they are named by one letter or a group of letters, such as type A, type X, type Y, type ZSM, etc. [115].



(a)

(b)

(c)

Figure 9. (a) Structure of activated carbon; (b) Array of SiO4 in silica gel; (c) Crystal cell unit of zeolite: left: crystal cell unit of type A zeolite; right: crystal cell unit of type X, Y seolity or faujasite [22,125].

Chemical adsorbents mainly include metal chlorides, metal hydrides, and metal oxides [22]. The metal chlorides for adsorption refrigeration are mainly calcium chloride, strontium chloride, magnesium chloride and barium chloride [126]. The adsorption reaction between metal chlorides and refrigerants is a complexation reaction, and the complex compound is also called coordinated compound [127]. Salt hydrides and metal hydrides can be utilized for adsorption refrigeration; in the adsorption process, H atoms become protons when they enter the space between hexagonal crystal lattices. When the metal oxides are used as adsorbents in adsorption heat pump [111,128,129], oxygen is the refrigerant. On the surface of metal oxides, the elements which influence the adsorption performance are the coordination number of the metal ion, the unsaturated degree of coordination, the direction of the chemical bond on the surface of the chemical material, the symmetrical characteristic of the transition metal ligand field, the number of d electrons of the transition metal ligand field, and the arrangement of the active centres [130].

Composite adsorbents are developed and studied with mainly two goals [22]: to improve heat and mass transfer performance of chemical adsorbents [131], especially due to the swelling and agglomeration phenomena, and to increase the adsorption quantity of physical adsorbents [132]. The composite adsorbents made from porous media and chemical sorbents are commonly a combination of metal chlorides and activated carbon, or activated carbon fibre, or expanded graphite, or silica gel or zeolite.

On the other hand, the common refrigerants used in adsorption systems are ammonia, water, and methanol [22]. Hydrogen and oxygen are examples of other refrigerants that can be adopted in adsorption refrigeration systems. Other refrigerants, as R134a, R22, R407c and ethanol can be utilized if activated carbon or activated carbon fibre is the sorbent.

Table 8 presents a summary of conventional working pairs for solid-gas sorption [1,5,9,19,22].

Table 8. Summary of conventional working pairs for solid-gas sorption [1,5,9,19,22]

	Working pair	Heat source temperature	Application	Advantages	Disadvantages
Physical sorption working pairs	Silica gel/water	60-85 ºC	air-conditioning	high latent heat of vaporization of water, suitable for solar-powered cooling systems and desiccant cooling systems, the reutilization of low-temperature waste heat	unsuitable for the refrigeration application below 0 ºC, vacuum system and it is very sensitive to the leakage risk
	Zeolite/water	>150-200 ºC	air-conditioning	high latent heat of vaporization of water, suitable for the reutilization of high-temperature exhaust gas and desiccant cooling systems	only used for the refrigeration higher than 0 ºC, high desorption temperature
	AC/AC fibre/methanol	80-110 ºC	air-conditioning, refrigeration, ice-making	large sorption capacity, low adsorption heat, suitable for solar-powered refrigeration systems	low latent heat of vaporization of methanol, unsuitable for heat source temperature higher than 120 ºC
	AC/AC fibre/ammonia	>130-150 ºC	air-conditioning, refrigeration, ice-making	good mass transfer, relative high latent heat of vaporization of ammonia, wide range of heat source temperature	toxicity and pungent smells of ammonia, low sorption capacity, the incompatibility with copper used in heat exchanger
	AC/AC fibre/R134a	>90-100 ºC	air-conditioning, refrigeration, ice-making	good mass transfer, wide range of heat source temperature	low sorption capacity and cooling power per mass unit, low latent heat of vaporization of refrigerant, relative high GWP value
Thermochemical sorption working pairs	Metal chloride/bromide/iodide-ammonia*	>50-350 ºC^{+}	air-conditioning, refrigeration, ice-making, deep-freezing	high sorption capacity per mass of sorbent, wider range of heat source temperature, suitable for refrigeration and heat transformer.	the swelling and agglomeration of salt, poor heat and mass transfer, reduction in the sorption capacity after many cycles
	Metal oxides-oxygen/water/carbon dioxide**	>150-1000 ºC^{+}	refrigeration, cryogenic, high-temperature heat pump	high sorption capacity, wider range of heat source temperature, suitable for cryogenic conditions and high-temperature heat pump	the swelling and agglomeration of salt, poor heat and mass transfer, reduction in sorption capacity after many cycles, unsuitable for low-temperature heat source due to their high desorption temperature
	Metal	>110-400	air-conditioning,	fast sorption kinetics, high reaction	low specific cooling power per mass of sorbent,

	hydrides-hydrogen***	ºC[+]	refrigeration, deep-freezing, heat pump	heat for heat pump, high packed density, wider range of heat source temperature	the swelling and agglomeration of salt, poor thermal conductivity after many cycles
Composite sorption working pairs	Silica gel/metal chlorides/water*[4]	60-85 ºC	air-conditioning	high sorption capacity per mass of composite sorbent, high latent heat of vaporization of water, suitable for solar-powered cooling systems and desiccant cooling systems	only used for the refrigeration higher than 0 ºC, poor heat transfer of composite sorbent, and the risk of salt solution leakage from composite sorbent
	Metal chlorides/porous matrix-ammonia*[5]	>50-350 ºC[+]	air-conditioning, refrigeration, ice-making, deep-freezing, heat pump, heat transformer	high sorption capacity per mass of composite sorbent, good heat and mass transfer of composite sorbent, wider range of heat source temperature	the complex fabrication of composite sorbent using mixture or impregnation and consolidation, the incompatibility with the conventional material of copper used in heat exchanger

* The common metal chlorides include calcium chloride, barium chloride strontium chloride, magnesium chloride, nickel chloride, etc.
** The common metal oxides include calcium oxide, lead oxide, magnesium oxide, titanium oxide, etc.
*** The common metal hydrides include advanced porous metal hydrides (PMHs) and the misch metal (Mm) matrix alloys containing Ni, Fe, La, Al, H, etc.
*[4] The common metal chlorides include lithium chloride and calcium chloride, etc.
*[5] The common porous matrix includes activated carbon, expanded graphite, activated carbon fibers, vermiculite, metallic foams, etc.
[+] driving temperature depends on different working pairs

Table 9 shows a comparison between adsorption working pairs; COP, SCP, delivered evaporation temperature, and required driving source temperature are presented. COP of the adsorption cooling systems achieved a maximum of 0.83 when employing metal hydrides/hydrogen pair, while the maximum SCP is achieved with AC/ammonia pair. It can be seen that most of the adsorption cooling systems are good to be driven by a low-grade heat source temperature lower than 100 ºC. On the other hand, the lowest evaporator temperature is -50 ºC, produced with the metal hydrides/hydrogen pair (since the hydrogen has a very low normal boiling temperature, -252.87 ºC). There is no ideal working pair for adsorption cooling applications, but every system has an advantage over the other; therefore, the working pair should be chosen based on the application, from the point of interest of low evaporator temperature, or low driving temperature, or high SCP, or high COP.

Table 9. Sorbent and system properties and performance

Sorption pair/system	COP	SCP (W/kg)	Te (ºC)	Td (ºC)	Thermal conductivity (W/m·kg)	Bulk density (kg/m^3)	Characteristics	Comments	Reference
Silica gel/water	0.61	208	12	82	---	---	---	---	[22,23,133-137]
	0.4	85	10	---	---	---	Split heat pipe type evaporator	Data obtained experimentally	[22,109,138]
	0.36	---	10	55	---	---	---	---	[26,139]
	0.5	---	15	85	---	---	---	---	[26,140]
	0.50	---	10	84	---	---	---	---	[26,141]
	0.41	---	2	80	---	---	x_{weak}=0.03 kg/kg; x_{strong}=0.125 kg/kg	Data calculated	[26]
	0.31	---	2	95	---	---	x_{weak}=0.03 kg/kg; x_{strong}=0.0.80 kg/kg	Data calculated	[26]
	0.26	---	2	110	---	--	x_{weak}=0.03 kg/kg; x_{strong}=0.040 kg/kg	Data calculated	[26]
	---	2800 kJ/kg	---	---	---	1000	Used mostly for descent cooling	---	[5]
	0.20-0.30	---	---	---	---	---	Solar adsorption with 170 m^2 of vacuum tube collector	---	[5,142]
	0.10-0.13	---	---	---	---	---	---	---	[5,143]
	0.25	---	14	55	---	---	Amount of adsorbent is allocated to adsorbent beds and effect of mass ration is investigated	---	[21,144]
	0.3-0.65	---	14	60	---	---	Effect of silica gel mass on COP is investigated	---	[21,145]
	---	---	5	100	---	---	Solar energy driven adsorption heat pumps are studied	---	[21,146]
	0.6	---	---	---	---	---	AHP system is applied on air-conditioning of buildings	---	[21,147]
	0.5	---	-10	100	---	---	Lab scale AHP system is constructed	---	[21,148]
	0.6	---	10	80	---	---	AHP system is applied on air-conditioning of buildings	---	[21,149]
	0.5	---	10 to 20	80-95	---	---	Small capacity AHP is constructed and tested for heating and cooling applications	---	[21,150]
	---	---	15 to 20	95	---	---	Compact solid sorption heat pump is developed and tested	---	[21,151]
	0.117-0.143	---	14	55-65	---	---	Development of hybrid desiccant cooling system combined with two stage adsorption chiller	---	[21,152]
	0.32-0.4	---	15.1	55-67	---	---	Novel adsorption chiller is developed and tested	---	[21,153]
	0.4	---	15	60-92	---	---	Micro adsorption chiller is applied on natural gas and LPG power cogeneration system	---	[21,154]
	0.427-	---	---	---	---	---	Effects of variation of heat source on COP of AHP	---	[21,155]

	0.434						are investigated		
	---	---	25	100	---	---	Development of micro-refrigeration system	---	[21,156]
	0.16	---	---	---	---	---	2.05 MJ/day/m2 solar ice making	---	[20,157]
	0.36	---	---	---	---	---	3.2 kW/unit solar chilled water	---	[20,139]
	0.28	---	---	---	---	---	12.0 kW/unit solar chilled water	---	[20,158]
	0.35-0.60	---	---	---	---	---	15 kWm^3 solar chilled water	---	[20,140]
	0.3-0.6	---	---	---	---	---	20 W/kg solar chilled water	---	[20,159]
	0.33-0.5	---	---	---	---	---	91.7-171.8 W/kg solar chilled water	---	[20,160]
	---	1000	30	150	---	---	---	---	[25,139]
	---	600	20	130	---	---	---	---	[161,162]
	0.49	84	80	14	---	---	---	---	[163]
	0.37	14	85	12.2	---	---			[164]
	0.42	270	10	80	14	14	---	---	[164]
	0.32	144	30	85	---	---	---	---	[164]
	0.36-0.66	132-164	3	200	---	---	---	---	[137]
	0.37-0.45	---	12.2	85	---	---	---	---	[165]
	0.42	270	10	80	---	---	---	---	[160]
	0.32	144	30	85	---	---	---	---	[164]
	0.36	241	14	50-70	---	---	---	---	[139]
	0.27	138	14	55	---	---	---	---	[166]
	0.24	168	14	55	---	---	---	---	[144]
	0.27	86	14	70	---	---	---	---	[144]
	0.27	71	14	80	---	---	---	---	[167]
	0.14	---	12	40	---	---	---	---	[168]
	0.19	28	12	50	---	---	---	---	[169]
	0.13	---	14	50	---	---	---	---	[170]
	0.14-0.23	84-190	14	50-60	---	---	---	---	[171]
Silica gel/water – zeolite/water	---	---	---	---	---	---	Comparison of adsorbents (zeolite & silica gel) due to their energy storage capacity	---	[21,172]
Silica gel and chlorides/water	0.8	---	7	70	---	---	---	---	[23,173]

Silica gel-CaCl2/water	0.30	20	150	---	---	---	---	---	[26,159]
Silica gel/methanol	---	1000-1500 kJ/kg	---	---	---	791	Suitable for temperature less than 200 ºC	---	[5,17]
	0.3	---	0	85	---	---	Solar-hybrid powered AHP system is designed and applied for decentralized cold storage of agricultural products	---	[21,174]
Silica gel and chlorides/methanol	0.33	---	-10	47	---	---	---	---	[23,175,176]
Silica gel/air	0.935	---	29	90	---	---	---	---	[26,177]
	0.935	---	25	80	---	---	---	---	[26,48]
Activated alumina/water	---	3000 kJ/kg	---	---	---	1000	Water is applicable except for very low operation pressure	---	[5,17]
Zeolite/water	0.4	600	6.5	350	---	---	---	---	[23,178 -181]
	0.9	125*	5	---	---	---	Intermittent convective thermal wave cycle	Data calculated	[22,182]
	---	3300-4200 kJ/kg	--	---	---	1000	Natural zeolite as lower values than synthetic zeolite	---	[5,17]
	0.11	---	1	118	---	---	Solar adsorption with 20 m^2 of flat plate collector	---	[5,183]
	0.10-0.12	---	---	---	---	---	Solar adsorption with 1.5 m^2 of flat plate collector	---	[5,184,185]
	0.34	---	27	123	---	---	Natural zeolite seem as alternative adsorbent for adsorption heat pump system	---	[21,186]
	0.34	---	25	200	---	---	Natural zeolite seem as alternative adsorbent for adsorption heat pump system	---	[21,187]
	0.74	---	4	230	---	---	The bed design enhanced mass and heat transfer rate	---	[21,188]
	Single 0.3-0.38, double 0.5-0.73	---	3	120-360	---	---	Effect of regeneration system temperature on COP of system	---	[21,181]
	---	---	3	290	---	---	Influence of physical properties of heat transfer fluid on AHP system	---	[21,189]
	---	---	3	210	---	---	Optimum coating thickness is determined	---	[21,190]
	0.3	---	2	150	---	--	Lighter adsorption heat pump system can be obtained with using polymeric heat exchanger tubes	---	[21,191]
	0.94-	---	0	350	--	---	Exergy analysis of four cascades cycled heat pump	---	[21,192]

	1.008						systems is performed		
	0.46	---	7	200	---	---	Open cell cooper foam is applied on AHP for improving heat transfer properties	---	[21,193]
	---	---	---	---	---	---	Optimization of zeolite coating process on stainless steel tube	---	[21,194]
	---	---	82	103	---	---	Waste heat of evaporation desalination process is used for cooling purposes by AHP	---	[21,195]
	---	---	2	135	---	---	Optimum coating thickness is determined	---	[21,196]
	---	---	2	151	---	---	The effects of thermal and mass diffusivities on the performance of AHP is studied	---	[21,197]
	---	---	---	---	---	---	Optimum thickness is determined for zeolite type (13X and 4A)	---	[21,198]
	---	---	---	---	---	---	Solar energy driven AHP is designed	---	[21,199]
	---	---	2	---	---	---	Solar powered AHP is used for ice-making	---	[21,200]
	---	---	2	151	---	---	Effect of metal mass on the performance of AHP	---	[21,201]
	1.4	---	---	96	---	---	AHP system is applied on air-conditioning of buildings	---	[21,202]
	0.43-1.04	---	10 to 40	150	---	---	One of the first applications	---	[21,203]
	0.6-1.6	---	---	---	---	---	36-144 W/kg solar air conditioning	---	[20,204]
	0.41	---	---	---	---	---	97 W/kg solar air conditioning	---	[20,205]
	0.38	---	---	---	---	---	25.7 W/kg solar air conditioning	---	[20,206]
	0.20-0.21	---	---	---	---	---	21.4-30 W/kg solar air conditioning	---	[20,207]
	0.44	48.8	6	200	---	---	---	---	[208]
Zeolite NaX/water	0.39-1.03	---	3	200	---	---	---	---	[181]
	0.44-0.47	48.8-52	6	200	---	---	---	---	[209]
Zeolite/water/carbon/methanol	1.06	---	25	220 for zeolite bed, 100 for carbon bed	---	---	Heat required during regeneration of carbon bed is provided from zeolite beds	---	[21,161]
Zeolite and foam aluminium/ water	0.55	500	10	250	---	---	---	---	[23,162]

Zeolite/ammonia	---	4000-6000 kJ/kg	---	---	---	681	---	---	[5]
Zeolite/methanol	---	2300-2600 kJ/kg	---	---	---	791	---	---	[5]
	1.34	---	-5	155	---	---	Lab apparatus is constructed.	---	[21,210]
Zeolite 4A	---	1250 kJ/kg	30	350	---	---	---	---	[25,139]
Zeolite 5A	---	1200 kJ/kg	30	350	---	---	---	---	[25,139]
Zeolite 13X/water	---	---	10	150	---	---	Polyaniline/zeolite composite is prepared for enhancement of heat transfer of adsorbent bed	---	[21,211]
	---	1290 kJ/kg	30	350	---	---	---	---	[25,139]
	---	930 kJ/kg	20	300	---	---	---	---	[25,139]
Zeolite MgA	---	800	60	250	---	---	---	---	[25,139]
Zeolite/CO_2	---	---	0	-78.15	---	---	---	---	[212,213]
Zeolite /N_2	---	---	0	-195.8	---	---	---	---	[212]
Zeolite 13X-LiBr/water	0.33	---	12 to 6	110	---	---	Zeolite/water adsorption system combined LiBr/water absorption system for providing continuous system	---	[21,214]
Graphite foams	---	---	---	---	100-150	---	---	---	[9,215]
AC/water	0.05	---	---	---	---	---	Solar adsorption with 2 m^2 of flat plate collector	---	[5,216]
AC/methanol	0.114	---	---	---	---	---	Adsorptive solar refrigeration system is simulated	---	[21,217]
	0.12	---	-10	100	---	---	Solar powered AHP is used for ice-making	---	[21,218]
	0.12	---	---	---	---	---	6 kg/day/m2 solar ice making	---	[20,219]
	---	---	---	---	---	---	Dynamic simulation of AHP is studied with zeolite coated adsorbent bed	---	[21,220]
		590	20	140			---	---	[25,139]
	0.5	-10	100	---	---	---	Dynamic analysis of heat recovery process for AHP	---	[21,221]
	0.12-0.14	---	---	---	---	---	5-6 kg/day/m2 solar ice making	---	[20,222]
	0.13-0.15	---	---	---	---	---	6-7 kg/day/m2 solar ice making	---	[20,223]
	0.18	---	---	---	---	---	27 W/kg solar ice making	---	[20,224]
	0.4	---	---	---	---	---	73.1 W/unit solar chilled water	---	[20,225]
	0.47	148	10	100	---	---	---	---	[209,226]
AC+blackened steel/methanol	0.16	---	---	---	---	---	9.4 kg/day/m2 solar ice making	---	[20,227]

AC/ammonia	0.61	2000	-5	100	---	---	---	---	[23,106,228-232]
	---	1000	8	---	---	---	Convective thermal wave cycle	Data calculated	[22,101]
	0.67	557	3	---	---	---	Convective thermal wave cycle	Data calculated	[22,234]
	Cooling 0.36, heating 1.1-1.15	---	---	---	---	---	Two ton solid sorption heat pump system is built and tested for cooling and heating	---	[21,235]
	0.05	---	---	---	---	---	Solar adsorption with 1 m^2 of flat plate collector	---	[5,236]
	0.42-1.19	---	---	---	---	---	Solar air conditioning	---	[20,237]
	0.2	---	---	---	---	---	600 W/kg solar air conditioning	---	[20,238]
	0.10	---	---	---	---	---	35 W/kg solar ice making	---	[20,229]
AC-CaCl2/ammonia	0.41	731	-15	---	---	---	Composite adsorbent, heat pipe type heating and cooling	Data obtained experimentally	[22,114,239]
	0.36	627.7	-25	---	---	---	Composite adsorbent, heat pipe type heating and cooling	Data obtained experimentally	[22,114,239]
	---	---	---	---	---	---	Ammonia adsorption behaviour on new adsorbent composite materials	---	[21,240]
	0.36	---	-20	135	---	---	Ice-making system uses heat pipe principle to perform the heating and cooling process for adsorber	---	[21,241]
	---	---	---	95	---	---	Experimental and numerical simulation of water vapor adsorption behaviour on different adsorbents	---	[21,242]
	0.39	---	---	---	---	---	770 W/kg solar ice making	---	[20,243]
	0.26	528	-19	114	---	---	---	---	[243]
	0.23	409.1	-18.9	160	---	---	---	---	[244,245]
	0.26	528	-10	145	---	---	---	---	[245]
	0.23-0.27	409.1-486.5	-18.9	160	---	---	---	---	[244]
	0.14	---	-19.7	103	---	---	---	---	[246]
AC fiber-CaCl2/ammonia	0.6	330	1	---	---	---	Composite adsorbent, heat pipe heating	Data obtained experimentally	[22,122]
AC/H_2	---	---	30	-252.87	---	---	---	---	[247,248]
AC/HFC refrigerant	0.43	---	-60	150	---	---	System requires operating pressure about 8 bars for HFC as adsorbate	---	[21,249]
CaCl2/methanol	---	1800-2000 kJ/kg	---	---	---	791	Used for cooling	---	[5]
SrCl2/ammonia	0.32	230	-10	---	---	---	Single-effect system	Data obtained experimentally	[22,250]

(MnCl2-NiCl2)/ammonia	0.4	70*	-25	---	---	---	Double-effect system	Data calculated	[22,250]
AC/methanol	0.78	16	15	90	---	---	---	---	[23,251-253]
	0.10-0.12	---	-3	110	---	---	Solar adsorption with 6 m^2 of flat plate collector	---	[5,184]
	0.10-0.12	---	-6	70-78	---	---	Solar adsorption with 6 m^2 of flat plate collector	---	[5,17]
	0.38	---	-20 to +15	40-100	---	---	Mass transfer is enhanced by using activated carbon fibre	---	[21,254]
	0.41	---	15	86	---	---	Compared two bed scheme with four-bed scheme that improves the recovery efficiency by about 70%	---	[21,255]
	0.55-0.61	140-190	40	140-150	---	---	---	---	[136]
AC/ethanol	0.8	---	3	80	---	---	---	---	[23,256,257]
AC/N_2	---	---	30	-195.8	---	---	---	---	[258]
Consolidated zeolite 4A	---	312	---	---	0.3	960	---	---	[9,260,261]
Consolidated zeolite 4A + adhesive bond to wall	---	432	---	---	0.3	960	---	---	[9,260,261]
Consolidated zeolite 13X	---	---	---	---	0.58	---	---	---	[9,262]
Consolidated carbon	---	16	---	---	0.27-0.34	---	---	---	[9,253]
Consolidated carbon/carbon fibre + aluminium fins	---	446	---	---	---	---	---	---	[9,263]
Consolidated carbon/methanol	0.1	13	---	---	---	---	---	---	[9,264]
Consolidated	1.4	400	---	---	---	---	---	---	[9,265]

carbon/methanol shell and plates finned tube									
SWS/water	---	---	---	---	0.1-0.3	---	---	---	[9,266]
	0.17-0.48	---	10	90	---	---	Advanced solid sorption chiller based on coated heat exchanger with SWS is tested and achieved a cycle time of 20-40 min	---	[21,267]
SWS/water-zeolite/water	0.28	---	-5	122	---	---	Hybrid adsorption cooling unit for vaccine storage utilizing solar energy as main power supply and a gas burner as an alternative power supply is developed and tested	---	[21,268]
Granular carbon	---	---	---	---	0.1	500	---	---	[9,269]
Expanded graphite/metal chloride	---	---	---	---	10-40	---	---	---	[9,121]
Expanded graphite/silica gel	---	40	---	---	10-20	---	---	---	[9,270,271]
Graphite/silica gel/water	---	35*	3	---	---	---	Composite adsorbent to intensify the heat transfer	Data obtained experimentally	[22,272]
Graphite/CaCl2/ammonia	0.3	1000	-15	---	---	---	Composite adsorbert	Data calculated	[22,272]
Expanded graphite/zeolite	---	---	---	---	4-17	---	---	---	[9,273]
Expanded graphite/zeolite 13X	0.9	35	---	---	5-15	---	---	---	[9,274]
Charcoal/ethane	---	1000-1200 kJ/kg	---	---	---	---	Reacts at approximate 100ºC	---	[17]
Charcoal/ammonia	---	2000-2700 kJ/kg	---	---	---	---	---	---	[17]
Carbon/ammonia	1.20	---	-15	160	---	---	A new configuration provides the higher contact area between adsorbent and heat exchanger	---	[21,275]
	0.6-0.62	---	15	130-195	---	---	Computer simulation model of an isothermal carbon-ammonia AHP bed in MATLAB	---	[21,276]

	0.3	---	9.5	150	---	---	Experimental test of compact sorption generator prototype	---	[21,277]
Charcoal/water	---	2300-2700 kJ/kg	---	---	---	---	---	---	[17]
Carbon/water	0.95	---	0	250	---	---	Forced convection is used for improving mass transfer	---	[21,278]
Charcoal/methanol	---	1800-2000 kJ/kg	---	---	---	---	---	---	[17]
Carbon/methanol	---	---	9	110	---	---	The system is driven by waste heat exhausted from engine	---	[21,279]
	---	---	7	90	---	---	Influence of adsorption and desorption capacity on operating process for AHP is studied	---	[21,280]
Carbon-methanol/zeolite/water carbon-ammonia	---	---	---	---	---	---	Common used adsorbent-adsorbate pairs are investigaged	---	[21,281]
Charcoal/ethanol	---	1200-1400 kJ/kg	---	---	---	---	---	---	[17]
Carbon fiber/ethanol	---	---	---	80	---	---	Adsorbent bed generally has heavy weight. Adsorber must be designed lightweight to reduce sensible heat losses from body	---	[21,282]
Monolithic carbon	---	---	---	---	0.6	750	---	---	[9,283]
	---	---	---	---	0.33	713	---	---	[9,284]
	---	---	---	---	0.27-0.34	---	---	---	[9,253,285]
Monolithic carbon/plate heat exchanger (simulation)	---	2000	---	---	---	---	---	---	[9,106]
Monolithic carbon/aluminium laminate	---	200	---	---	20	---	---	---	[9,286]
Carbon matrix (carbide precursor)	---	---	---	---	2-10	---	---	---	[9,287]
Metal chloride/am	0.6	---	-10	52	---	---	---	---	[23,288,289]

monia									
Metal hydride/hydrogen	0.83	300	-50	85	---	---	---	---	[23,290-292]
	0.43	25*	-10	---	---	---	Thermal wave cycle	Data obtained experimentally	[22,293]
	---	2300-2600 kJ/kg	---	---	---	1000	Used for air-conditioning	---	[5]
Metal hydride	0.3	20	150	---	---	---	---	---	[26,294]
	0.33	1.5	130	---	---	---	---	---	[26,295]
	0.20	10	110	---	---	---	---	---	[26,296]
Metal oxides/water	---	78	100	200	---	---	---	---	[23,129,297]
Chlorides and porous media/ammonia	0.35	1200	-15	117.5	---	---	---	---	[23,231,272,298 --300]
MIL-101(Cr)	---	---	---	---	---	---	---	---	[23,301]
MIL-101(Cr)	---	---	---	---	---	---	---	---	[23]
MIL-101(Cr)	---	---	---	---	---	---	---	---	[23,302]
MIL-101(Fe)	---	---	---	---	---	---	---	---	[23,302]
MIL-101(Cr) (X=Cl)	---	---	---	---	---	---	---	---	[23,303]
HKUST-1	---	---	---	---	---	---	---	---	[23,303]
HKUST-1	---	---	---	---	---	---	---	---	[23,303]
ISE-1	---	---	---	---	---	---	---	---	[23,303]
Basolite^{TM} C300	---	---	---	---	---	---	---	---	[23,304]
Basolite^{TM} A100	---	---	---	---	---	---	---	---	[23]
Basolite^{TM} F300	---	---	---	---	---	---	---	---	[23,302]
$CaCl_2$/Expanded graphite/NH_3	0.38	---	-15.6	25	---	---	---	---	[305]
	0.27	422	-15.6	140	---	---	---	---	[306]

$NiCl_2$-NH_3/$MnCl_2$ - NH_3	0.60	---	-10	290	---	---	---	---	[307]
$FeCl_2$-NH_3/$SrCl_2$-NH_3	0.7	---	-10	213	---	---	---	---	[307]
$NiCl_2$-NH_3/$MnCl_2$ - NH_3	0.58	---	169	258	---	---	---	---	[308]
$FeCl_2$-NH_3/$CaCl_2$-NH_3	0.7	---	102	261	---	---	---	---	[308]
$NiCl_2$-NH_3/$MnCl_2$ - NH_3	0.38	---	190	275	---	---	---	---	[309]
$NiCl_2$-NH_3/$MnCl_2$ - NH_3-$SrCl_2$- NH_3	0.88	---	122	245	---	---	---	---	[310]
$NiCl_2$-$BaCl_2$-NH_3	0.47	---	5	268	---	---	---	---	[309]
$MnCl_2$-$BaCl_2$-NH_3	0.52	---	10	180	---	---	---	---	[311]
	0.64	---	10	180	---	---	---	---	[312]
	0.70	225	15	160	---	---	---	---	[313]
$NiCl_2$-$CaCl_2$-$BaCl_2$	1.29	---	30	253	---	---	---	---	[314]
$FeCl_2$-$CaCl_2$-$BaCl_2$	1.5	---	30	218	---	---	---	---	[314]
$NiCl_2$-$MnCl_2$-$BaCl_2$	1.10	---	155	265	---	---	---	---	[314]
	1.0-1.2	---	30	260	---	---	---	---	[315]

*The SCP in the original literature was calculated based on the total cycle time, with adsorption and desorption of same length. To allow a fair comparison, the original value should be multiplied by two.

Table 9 shows the newly presented adsorbent-refrigerant pair, developed to achieve optimized adsorption working systems. Among of these pairs, AC/R134a has a relatively high adsorption capacity and low evaporation temperature (-26.55 ºC). But the problem with R134a that it has a high global worming potential value (1300). The lowest adsorption capacity is for the pair of AC/N_2 and the highest one is for the pair of AC/R134a. Although the AC/N_2 has a relatively low adsorption capacity, it has the lowest boiling temperature (-195.8 ºC) which means it will be good to be used in refrigeration applications. AC/diethyl ether has a relatively high adsorption capacity of about 1.63 but it has the disadvantages of working at vacuum pressure and a relatively high boiling temperature of about 34 ºC.

Heat of adsorption can be derived from adsorption isotherms (Figure 4), referred to as isosteric heat (the energy released in the adsorption process), or as the differential heat of adsorption determined experimentally using a calorimetric method (Table 9) [17]. To understand the adsorption process, the adsorption equilibria are introduced to describe the adsorption process and several state equations known as isotherms of adsorption are proposed [318,319]. Several basic theories have been proposed and used to define the main isotherms of an adsorption process, the Henry's law [320], the Langmuir's approach [321], the Gibbs' theory, and the adsorption potential theory; other recent equations have been developed recently and are presented in Table 10.

Table 10.Thermodynamic reaction values of common metal chloride/bromide/iodide-ammonia sorption pairs [18,316,317]

Reactive salt	Reaction enthalpy (J/mol)	Reaction entropy (K/mol K)	Reaction coefficient *m*	Reaction coefficient *n*	Molar mass (g/mol)	Driving equilibrium temperature (T_C=30 ºC)
NH_4Cl	29.433	207.9	3	0	53.4	48
KI	32.015	219.8	4	0	166	36
LiBr	33.689	225.9	1	4	86.8	34
PbCl2	34.317	223.6	4.75	3.25	278	47
NaBr	35.363	225.2	5.25	0	102.9	51
CaI_2	35.991	229.3	2	6	293.8	45
LiCl	36.828	224.6	1	3	42.3	67
$PbBr_2$	37.665	229.4	2.5	3	367	60
$BaCl_2$	38.250	232.4	8	0	208.2	56
$PbCl_2$	39.339	230.1	1.25	2	178	72
$PbBr_2$	39.758	229.4	1	2	367	78
PbI_2	40.595	229.1	3	2	461	87
$CaCl_2$	41.013	230.1	4	4	110.8	87
NaI	39.339	224.5	4.5	0	149.9	90
$BaBr_2$	41.850	229.8	4	4	297.1	95
$SrCl_2$	41.432	228.6	7	1	158.4	96
$CaCl_2$	42.269	229.7	2	2	110.8	99
$BaBr_2$	42.687	230.7	2	2	297	100
LiCl	44.780	229.8	1	2	42.3	120
$SrBr_2$	45.617	229.3	6	2	247.4	130
BaI_2	46.454	231.6	2	4	391.1	130
BaI_2	47.291	230.3	2	2	391.1	142
$MnCl_2$	47.416	227.9	4	2	125.7	152
LiCl	48.128	230.6	1	1	42.3	148
$CaBr_2$	48.965	230.4	4	2	199.8	156
$ZnCl_2$	49.467	230.0	2	2	136.2	162
$FeCl_2$	54.266	227.8	4	2	126.6	186
SrI_2	52.731	230.5	4	2	341.4	188
$MnBr_2$	53.066	228.3	4	2	214.7	200
$CoCl_2$	53.987	227.9	4	2	94.3	210
$MgCl_2$	55.661	230.4	4	2	95.1	214
$FeBr_2$	55.828	228.1	4	2	215.6	226
BaI_2	56.079	235.0	2	0	391.1	199
CaI_2	58.590	231.	4	2	293.8	237
$CoBr_2$	58.590	227.5	4	2	218.7	253
$NiCl_2$	59.218	227.6.	4	2	129.5	259
MnI_2	59.301	227.4	4	2	308.7	260
FeI_2	60.683	227.5	4	2	309.6	272
$MgBr_2$	63.612	230.2	4	2	184.1	285
$NiBr_2$	64.240	227.2	4	2	218.5	306
NiI_2	65.453	224.1	4	2	312.5	334

Based on the reversible reaction: $Solid \cdot (n+m)NH_3 + \Delta H \leftrightarrow Solid \cdot nNH_3 + mNH_3(gas)$

A new class of microporous materials known as porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) emerged recently [24]. These materials possess unique features such as huge surface area, large pore volume, and an unprecedented geometric, chemical, and physicochemical variability, which are due to their tunable composition. With regard to the application in adsorption heat transformation processes, the main focus lies on water adsorption properties and storage capacities, which are strongly connected to the specific pore volume. Several compounds with large water uptakes up to 1.43 g/g have been identified. This is more

than four times the maximum loading of conventionally used zeolites. With ongoing development, the specific pore volumes have increased from 1 cm^3/g (MOF-5) up to more than 2 cm^3/g for MIL-101 [322]. In combination with increasing pore volumes, extremely high surface areas up to 5000 m^2/g have been reported for several MOFs. This has also started a discussion on the applied measurement methods, for example, the determination of the surface area by the BET method [323]. Another unique feature can be observed when dealing with the adsorption properties of MOFs. Some frameworks show geometric flexibility, that is, a reversible change in the structure and sometimes even in the physical properties in response to guest adsorption [324].

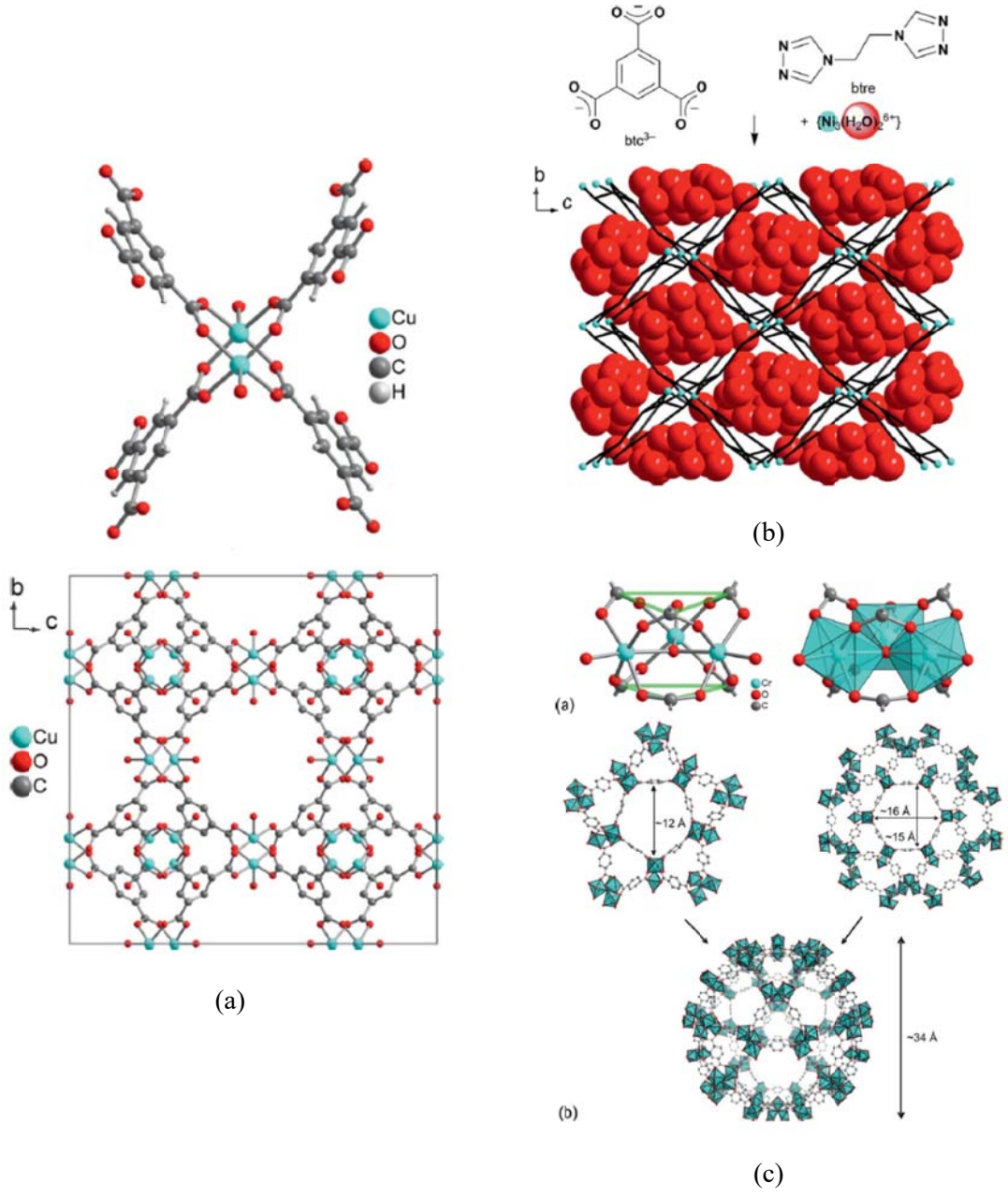


Figure 10. MOFs used in adsorption technologies [24]. (a) HKUST-1; (b) ISE-1; (c) MIL-101

Compared to traditional adsorbents used in heat pump applications, like zeolites or aluminophosphates, MOFs exhibit a much richer variety in terms of composition, pore structure, and topology. Another advantage is the mechanism of synthesis. For applications in periodically working heat pumps or adsorption chillers, the comparatively weak thermal and especially hydrothermal stability of MOFs can be a disadvanges and is the most critical issue [325]. The most crucial point for hydrothermal stability is the nature of the metal–ligand coordinative bond.

Among different solid sorption refrigeration cycles, two operating strategies have been proposed and adopted for the improvement of system performance. In the first strategy, working performance can be improved by enlarging the cycled mass of refrigerant during adsorption phase using mass recover process between different sorption beds. In the second strategy, working performance can be improved by reducing the heat consumption during desorption phase using heat recovery process between different sorption beds. Later, the two strategies are combined to improve system performance by enlarging cooling capacity and reducing heat consumption simultaneously. These advanced sorption refrigeration cycles can significantly improve the thermodynamic efficiency and thus enhance the working performance. On the other hand, some advanced solid sorption refrigeration cycles have been proposed to lower the driving temperature to extend the reutilization of low-grade thermal energy. A summary of the working pairs used in the different strategies are presented in Table 9. In comparison with the basic solid sorption refrigeration cycle, advanced sorption cycles can improve the working performance significantly by introducing better heat management and mass recovery, or can effectively decrease the driving heat source temperature by employing two/multi-stage desorption sorption cycle. For advanced solid sorption refrigeration cycle with heat management strategy, heat recovery process is proposed to improve the working performance by reducing the heat consumption during desorption phase. For advanced solid sorption refrigeration cycle with mass recovery strategy, the working performance can be improved by enlarging the cycled mass of refrigerant when mass recovery process is introduced between different sorption beds. For advanced mass and heat recovery sorption refrigeration cycle, the aforementioned heat recovery and mass recovery strategies are combined to improve the working performance by enhancing cooling capacity and reducing heat consumption simultaneously. For advanced combined double-way thermochemical sorption cycle, both adsorption refrigeration and resorption refrigeration processes are combined to improve the cooling capacity. For advanced two/multi-stage sorption refrigeration cycle, the purpose is to lower the driving regeneration temperature in order to widen the scope of the reutilization of low-grade thermal energy instead of improving working performance.

3. Sorption thermal energy storage

In the last decade, sorption storage has reached plenty of interest, especially because it is seen as high potential for long-term storage also known as seasonal storage. Nowadays, sorption storage technology and materials are still under research, but several prototypes are being tested bigger than lab scale. Different terminologies are found in the literature that might be confusing. Here, sorption storage technologies and materials are the focus of interest and comprise both chemical and physical adsorption and absorption as depicted in green in Figure 11.

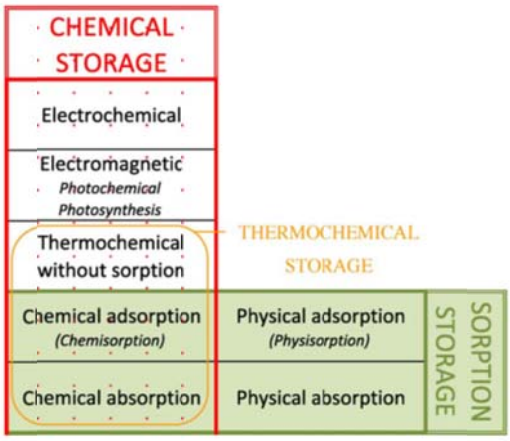


Figure 11. Sorption and chemical storage classification [327].

The concept of long-term energy storage or seasonal energy storage has become a research topic of interest in recent decades. Conventional storage methods can be sorted as short-term storage since heat input and output occur within an interval of several hours or days. Long-term energy storage is defined as storage systems designed to store energy for a few months or even a whole season to compensate for the seasonal offset of energy demand. In Table 11, the main characteristics with the aim of comparison of both short and long-term are shown for central solar heating systems. Sorption storage has been named as a potential technology for long-term solar energy storage, which is regarded as an efficient approach for making rational use of solar energy to achieve a considerable reduction of fossil fuel consumption and emission of CO_2 [6,328].

Table 11. Main characteristics of central solar heating systems with short and long-term storage (adapted from [6,328])

	Short-term storage	Long-term storage
Storage time	Hours to days	3 to 6 months
Minimum size	More than 30 apartments	More than 100 apartments
Yearly solar fraction	10 – 20 %	Over 50 %
Costs (Germany)	0.08 – 0.15 €/kWh	0.17 – 0.40 €/kWh/year
Flat plate collector (FPC) area	0.8 – 1.2 m^2/person	1.4 – 2.4 m^2/MWh annual heat demand
Storage volume	0.05 – 0.1 m^3 water/m^2 FPC	1.4 – 2.1 m^3 water/m^2 FPC

3.1. Technologies

Most of the technologies implementing sorption materials with storage are purposed for building comfort applications. Mainly air conditioning, heating, and DHW are the fulfilled requirements. Until now, these technologies have been designed tested as single equipment for a dwelling or as a buffer in district heating network.

3.1.1. Adsorption

Adsorption thermal energy storage is a promising technology that can provide an excellent solution for long-term thermal energy storage in a more compact and efficient way. Solar thermal energy or waste heat from several processes can be used to regenerate the adsorbent and promote the energy storage [5,326].

Reactors designed for sorption thermal energy storage systems based on gas-solid processes (physisorption and chemisorption) can be either open or closed. Also, the reactor can act as the container of all solid (integrated) or have it as another equipment, named separated.

Open systems, as the name suggests, are open to the environment. The gas involved is typically water vapour. For the sorption process during discharging is obtained directly from the ambient air, as shown in Figure 12 left, or in some cases from a moisture source such as a humidifier. This makes open systems weather dependent.

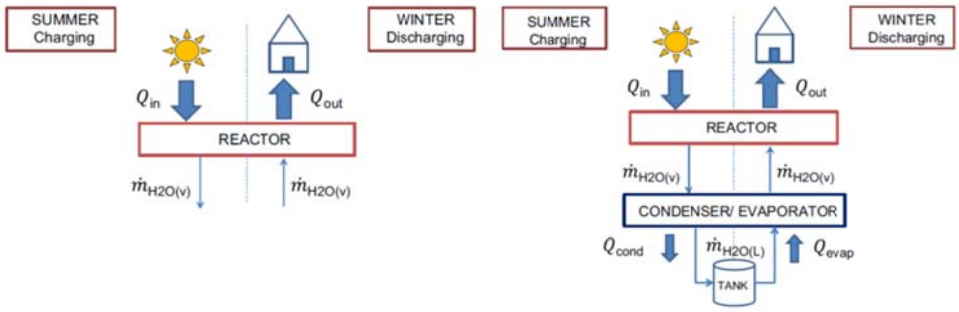


Figure 12. Open (left) vs. closed (right) systems with integrated reactor [329]

A closed adsorption system has no mass exchange with the environment and requires an evaporator/condenser for the working fluid, usually water, as can be seen in Figure 12 right. During the discharge process, evaporation of the working fluid is necessary and therefore a low heat source is required. Usually closed systems operate under vacuum conditions for optimal mass transport in the reactor [330]. When the working fluid is water the temperature of this heat source commonly needs to be at least at 5 ºC. It is not always mentioned how this heat should be supplied to the system, being still a key point that can make decide if as system is feasible or not [331].

On the contrary, the open system allows a simpler manufacturing of the reactor. The evaporator/condenser is not necessary, which does not affect negatively the apparent energy density of the storage system. Nevertheless, this working mode results in a flow of vapour and air through the bed, and the total flow is significantly higher than in the previous case. Thus, mass transfer must be carefully considered [332]. Moreover, although at the beginning of the reaction there is good vapour diffusion within these systems, as the time passes, the diffusion shows a decreasing trend and results in a corresponding drop in ΔT. This causes instability during heat generation, which is not evidenced in closed sorption systems. In closed cycles, the generated heat can be stored sensibly and the amount extracted can be altered by changing the parameters of the heat transfer fluids (e.g. mass flow rate) [333].

The closed sorption storage process is similar to that of chemical heat pumps with a major difference. A chemical heat pump works usually with two simultaneous circulations (continuous process) and needs therefore a condenser and an evaporator as well as a desorber and an ab/adsorber. Heat storage systems work in batch mode so that vessels are needed to store the products. In addition, the desorber might be used as an ab/adsorber and the condenser also as an evaporator [327].

A comparison between open and closed systems can be found in [327] and a numerical comparison has been published by Michel et al. [332], who concludes that for the closed system, the heat transfer is the main limitation, and a small increase of the thermal conductivity strongly improves the reaction rate. For example, a conductivity which is two times higher than the reference bed conductivity decreases the reaction time of about 14%. For the open system, the mass transfer is the main limitation and the hydration rate can be improved by acting on the bed permeability: doubling the permeability leads to a half reaction time. Both operating modes lead to close global performances. Thus, the open thermochemical reactor, which presents technical advantages (easier conception and management, lower cost, etc.), is a promising way to implement a thermochemical process as long-term heat storage.

Other authors also compared open and closed systems but for physical adsorption (zeolites 13X). The overall system energy and exergy efficiencies, respectively, are determined to be 50% and 9% for the closed storage, and 69% and 23% for the open storage. The results suggest that there is a significant margin for loss reduction and efficiency improvement for closed and open thermochemical storages, since the exergy efficiencies of both are significantly lower than the energy efficiencies [335].

Another possible configuration is to have an integrated or separate reactor. In the integrated reactor system (Figure 13b), the absorption/release of energy (reaction) occurs within the storage vessel, while the separate reactors (Figure 13a) concept consists in transporting the thermochemical material (TCM) from the storage vessel to the reactor and to another storage vessel, after reacting, as illustrated in Figure 13.

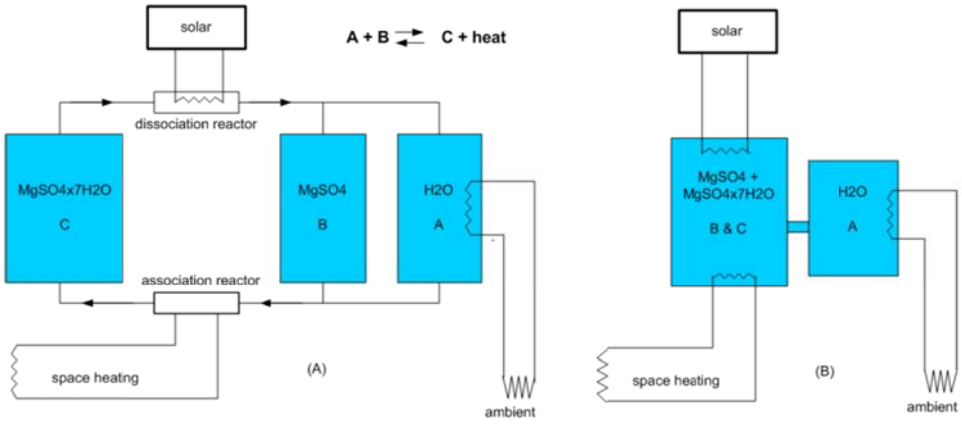


Figure 13. (a) Separated reactor, (b) reactor integrated in storage [336]

If the TCM material is a solid, preferably integrated reactors are used. This has the advantage that it is not necessary to transport the solid material, thus less power consumption. However,

for large storages such as seasonal storage, this also has disadvantages such as a larger sensible heat loss, since then the whole reactor content has to be heated up before dehydration occurs [336]. Furthermore, the required heat exchange area is much larger than for a separate reactor. In a separate reactor, it is possible to heat up only the required amount of TCM, thereby making the charging process much more efficient. Also, the heat and vapour transfer can be optimised within a separate reactor by stirring of the material.

a. Physisorption

An open adsorption system was designed as a buffer for a district heating network in Munich by ZAE Bayern, as shown in Figure 14. The buffer can store 1300 kWh for the heating during 14 h of a school building with a maximum power of 135 kW. This system, which stores without loss as long as wanted, is charged in periods when energy is available from the net in off-peak hours and can therefore be independent from the net at peak demand periods. It contains zeolite 13X and offers a storage density of 124 kWh/m^3 for heating and 100 kWh/m^3 for cooling with a COP of 0.9 and 0.86, respectively [327].

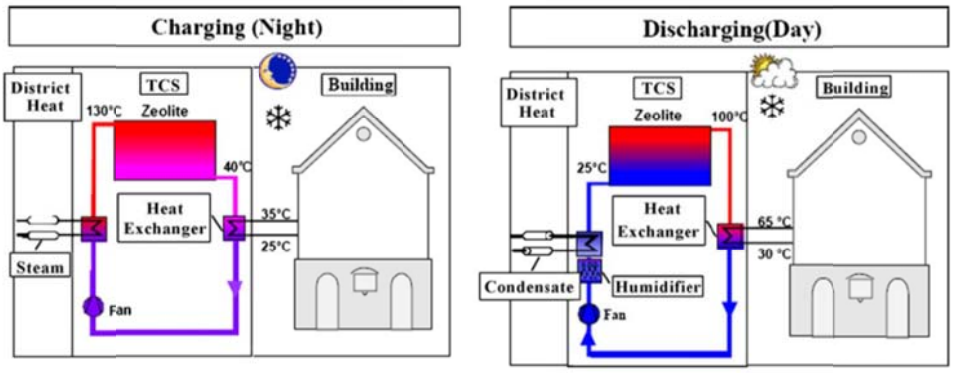


Figure 14. Open physisorption zeolites system on district heating net in Munich [337]

A prototype for heating and domestic hot water was built within HYDES project. The prototype consists on silica gel/H_2O as the sorption material combined with 20.4 m^2 of solar collectors. The charging (desorption) temperature is given by the solar collectors at 88 ºC. From the results it can be concluded that there is a 20% of losses regarding the storage density from the material to the system [327].

Another prototype based on silica gel/H_2O, in the frame of Modestore project, was built consists of a store filled with the storage material and equipped with an internal spiral heat exchanger, a water reservoir (900 l) and an additional small water reservoir with a heat exchanger which

serves as the evaporator or condenser. The tests of this prototype showed the unsuitability of the combination silica gel/H_2O for seasonal storage with flat-plate solar collectors (32 m^2) and available heat sinks which do not allow desorption under water content of 3% when the material has to operate in a water content range of 3–13% [327,329]. This significantly reduces the storage density of the material. In the pilot system an energy storage density of approximately 50 kWh/m^3 has been achieved. This is only 25 % of the total energy storage density of the theoretical value [327,329,338]. A schematic drawing of the sorption store is depicted in Figure 15.

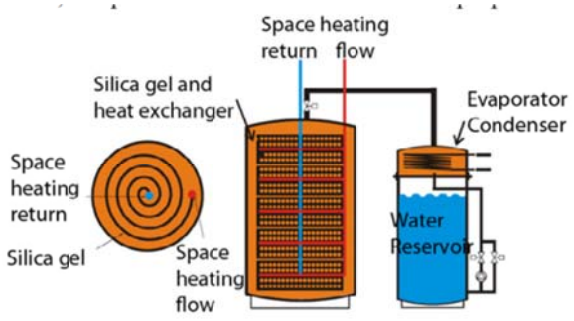


Figure 15 Modestore prototype based on silica gel/water as sorption material [329,338]

An open storage system containing zeolites was built in the frame of Monosorp project. Heat storage and removal from the store utilises the ventilation heat recovery system and moisture in the house [338,339]. The system was designed and tested showing promising results, however, the desorption temperature is very high, around 180 ºC, which makes the use of solar heat difficult with this concept [327].

In project SolSpaces prototype the aim is comparable to Monosorp and therefore the sorption system is integrated into an air heating system of a building which is equipped with a controlled ventilation system. The heat for desorption is provided by a collector field using air collectors. In this case the solar loop can be directly connected to the sorption store without the need for an air to water heat exchanger which was mandatory in the MonoSorp project. In contrast to the MonoSorp concept no zeolitic honeycomb monoliths are used as storage material but a packed bed of zeolite spheres.

Similar to the concepts of the MonoSorp and SolSpaces, CWS-NT-concept project is an open adsorption based on zeolites and salt as sorption material system using ambient or exhaust air to provide the humidity required for the discharging of the store. The thermochemical energy store works as a low power heat source and is connected to the combistore of the solar thermal system via the collector loop heat exchanger. The thermochemical energy store consists of a

material reservoir for the storage material and a reactor where the heat and mass transfer take place during the charging and discharging reaction. In the CWS-NT-concept, an external reactor concept has been realized where the storage material is separated from the reactor. This has the advantage that the reaction is reduced to only a small part of the total storage material amount at a time [338].

b. Chemisorption

An open system (atmospheric) instead of the close system, being this choice based on a previous techno-economical study done by Zondag et al. [340], was built and tested. The sorption material is $MgCl_2/H_2O$. The authors found that HCl was formed during the dehydration of $MgCl_2 \cdot 7H_2O$ at a temperature above 135 ºC. The formation of this gas not only degrades the storage material, but it is also strongly corrosive. Therefore, dehydration was limited to a temperature below 135 ºC. In addition, the over-hydration of $MgCl_2$ was avoided by impregnation into a carrier material (cellulose). The measured temperature lift was 15 ºC and a significant temperature rise was maintained in the bed after 24 hours. The calculated energy density of the material after 23 hours hydration was 0.14 MJ/kg [341].

An open chemisorption storage system for long-term solar heat storage with magnesium chloride on a carrier matrix as storage material was tested. The prototype reactor contains 15 litters of storage material. The temperature for dehydrating the material is set to 130 °C. During the hydration experiments a temperature lift of the airflow of 14 ºC from 50 °C to 64 °C has been measured in the material bed (relative humidity of the incoming airflow of 40 % at 25 °C). With a further improvement of the reactor design and the heat transfer in the air to water and air to air heat exchanger it is expected that the high energy density of the material of approximately 280 kWh/m³ can be technically used [338].

Another project, with a prototype based on sodium sulphide as sorption material was built and tested. The project aimed to improve the performance of a sodium sulphide/water chemical energy storage previously designed [342]. Key aspects of this concept are the modular design (the reactor, the evaporator and the condenser aligned into the same and straight line), the integrated oil bath that results in a low temperature source required (about 79.5 ºC) and the use of graphite additives. Graphite (30% in weight) is mixed with the sodium sulfide nanohydrated salt ($Na_2S \cdot 9H_2O$), reaching a COP of 1.11 (heating + cooling) [327].

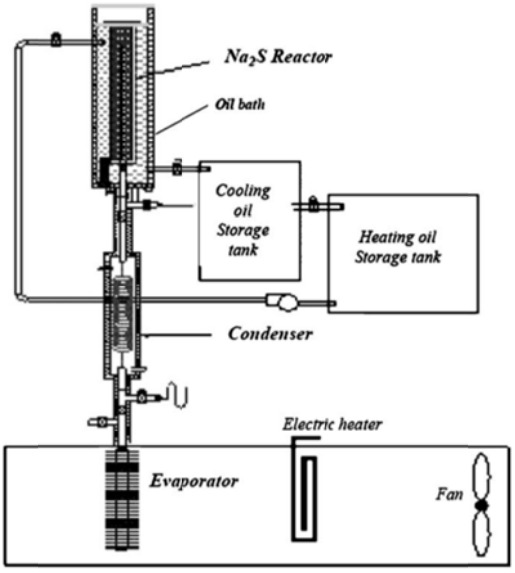


Figure 16. Scheme of the modular prototype based on Na_2S/H2O [343]

A prototype of modular energy storage system for cooling in buildings and industrial applications was developed and tested. The prototype is a closed spiro-tube heat exchanger containing sodium sulphide and water (Na_2S/H_2O) as the sorption material. Experimental results show a heat storage density of almost 1.1 kWh/kg and a cold storage of almost 0.7 kWh/kg [327]. The reported COP was 057. Some solutions have been used to minimize corrosion: use of stainless steel for vessels and copper. Moreover, due to the melting point at 83 ºC of the storage material, the upper limit for the condensation temperature was fixed at about 27 ºC. Nevertheless, the Na_2S was impregnated on fibrous cellulose to allow partial melting of the material without significant irreversibility. Peak cooling powers of 500 to 700 W were measured at evaporation temperature of 10 to 15 ºC, which remained relatively constant until all the water was evaporated. The measured maximum thermal storage capacities of the prototype were 3.2 kWh for heat and 2.1 kWh for cold [341].

A solar assisted sorption system using $SrBr_2$ was tested [344]. The system was designed for heating floor in winter or mid-season at 35 ºC and refreshing floor in summer at 18 ºC. $SrBr_2$ was mixed with expanded graphite and compacted. The reported mean cooling power was 48 $kW \cdot m^{-3}$ at the operating temperature of 80 ºC/35 ºC/18 ºC (summer) whereas the heating power in winter was 36 kW·m-3 at the operating temperature of 70 ºC/35 ºC/12 ºC (winter). The average powers were calculated from the experimental measurements obtained between 0 to 90 % of conversion. A prototype reactor that was able to store, with a complete reaction, 60 kWh and 40 kWh for heating and cooling respectively was built. In summer conditions (66 ºC/35-30 ºC/18 ºC), the mean refreshing power was -2.6 kW during the 14 h of the sorption period (0-92

%). On the other hand, in mid-summer conditions (70 ºC/12-30 ºC/12 ºC), the mean heating power was 2.2 kW during the first half of the sorption process (55 % conversion) [341].

A demonstration plant of the MERITS project containing numerous subsystems such as solar collectors, short term storage vessel, long term thermochemical storage modules (based on Na_2S), underfloor heating, ceiling cooling, and a domestic hot water system, was designed during the first two years of the project (2012-2014). All compartments, i.e. the heating & cooling systems, the technical space and the single family dwelling compartment complete with windows, ventilation and door, are integrated in a 45 ft. sea container and fully equipped with measuring equipment (Figure 17). The long term thermochemical storage system (heat battery) consists of 8 modules providing a loss-free design thermal energy storage capacity of 482 MJ delivered from the water and sodium sulphide (Na_2S) working-pair. As described in formula (1), the Na_2S is supposed to be cycling between the hemihydrate ($Na_2S \cdot ½H_2O$) and the pentahydrate ($Na_2S \cdot 5H_2O$). The ground source, simulated using a laboratory water bath, is used for evaporation and condensation. With an evaporator inlet temperature of 10°C, the TCS modules can provide a temperature of up to 60 °C to the short term buffer vessel, to anticipate the thermal demands during the winter period, with a constant power. After pre-testing the 8 thermochemical storage modules were introduced for winter testing in Warsaw, Poland. In a first test with a not yet optimized discharging control strategy an energy amount of 13.5 MJ could be discharged from one module [345,347].

Figure 17. Field Test Demonstrator 3D systems model (*left*), interior view of the energy processing compartment (*middle*), and Field Test Demonstration container during pre-testing in Lleida, Spain (*right*)

A novel thermochemical sorption cycle is proposed to upgrade the stored thermal energy by using a pressure-reducing desorption method during energy storage process and a temperature-lift adsorption technique during energy release process (Figure 18). Theoretical analysis showed that the proposed target-oriented thermochemical sorption heat transformer is effective for the integrated energy storage and energy upgrade, and the low-grade thermal energy can be upgraded from 87 ºC to 171 ºC using a group of sorption working pair $MnCl_2$-$CaCl_2$-NH_3.

Moreover, it can give the flexibility of deciding the temperature magnitude of energy upgrade by choosing appropriate sorption working pairs [246,348].

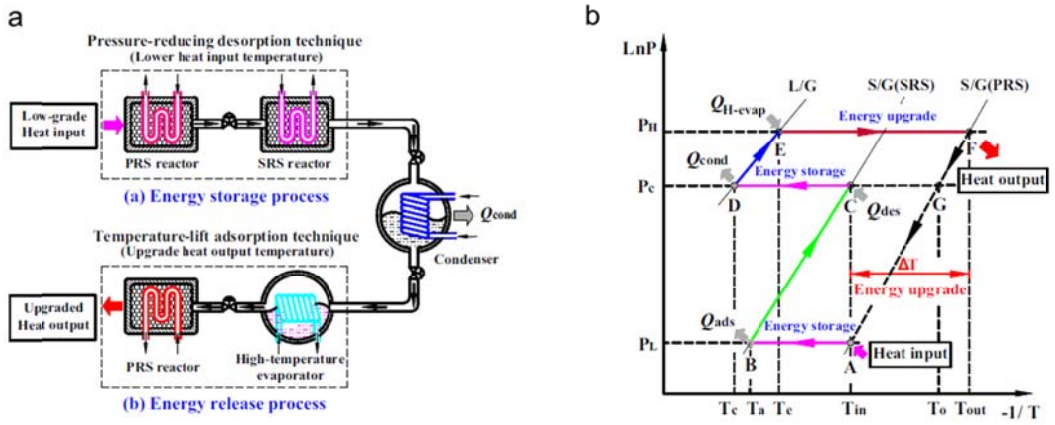


Figure 18. Schematic diagram of the novel target-oriented solid–gas chemical sorption heat transformer for the integrated energy storage and energy upgrade [348]. (a) Diagram of the physical arrangement of system components of the novel target-oriented solid-gas chemical sorption heat transformer and (b) Diagram of Clausius-Clapeyron

In the same direction, a dual-mode solid gas thermochemical sorption system is proposed for seasonal storage of solar thermal energy with little heat losses during long-term storage (Figure 19). In this case, the proposed system has two working modes which operate according to the different ambient temperature in winter. Defining the reactor mass ratio (R), as the mass of metallic parts of reactor heat exchanger (including vessels, tubes, fins, and so on) divided by the mass of the reactive salt in a solid-gas reactor, is employed to assess the effect of the thermal capacity of the metallic part of reactor on the COP for heat production (COP_h) and energy density of the proposed thermochemical sorption energy storage system.

At mass ratio of 5, global conversion of 0.85, and heat output temperature of 62 ºC, the COP_h and energy density obtained from the thermochemical seasonal energy storage process without internal heat recovery are 0.60 and 1043 kJ/kg_{salt} when the ambient temperature is 0 ºC in winter; these figures are 0.34 and 579 kJ/kg_{salt}, respectively, for the thermochemical seasonal energy storage process with internal heat recovery at an ambient temperature of 20 ºC [348].

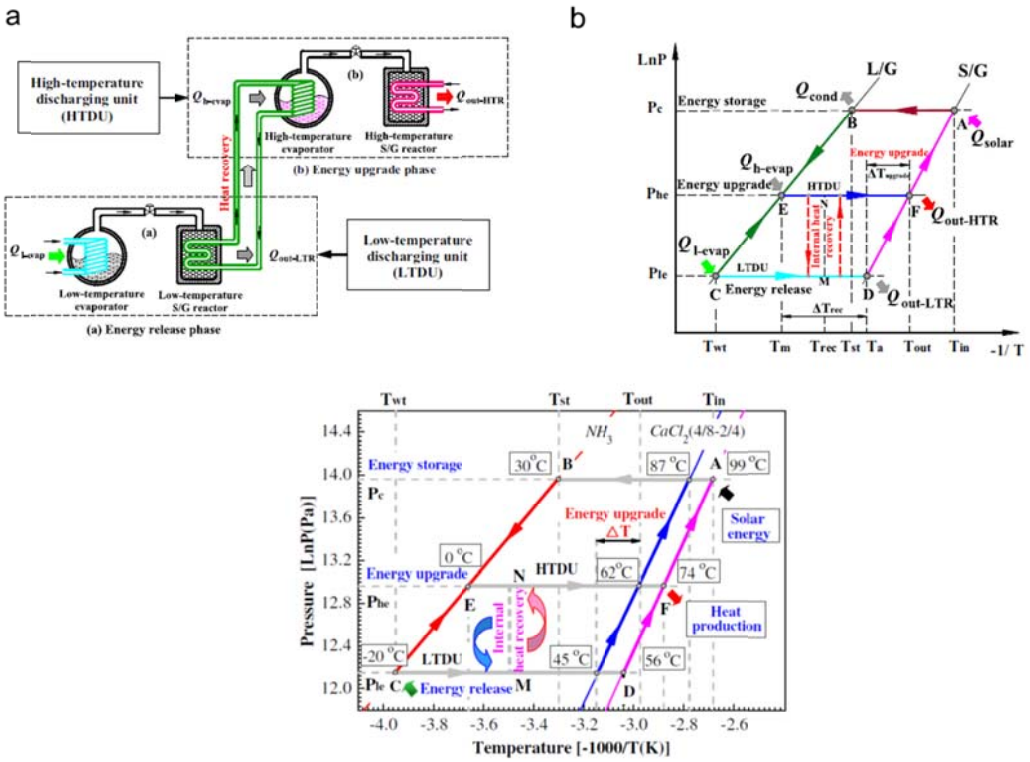


Figure 19. Schematic diagram of the dual-mode solid–gas chemical sorption system for seasonal storage of solar thermal energy [349]. (a)Internal heat recovery process between reactor in LTDU and evaporator in HTDU and Energy storage process: A-B; Energy upgrade process of HTDU: E-F; Energy release process of LTDU:C-D; Internal heat recovery process: M-N (b) Clausius-Clapeyron diagram (c) Clapeyron diagram of the integrated energy storage and energy upgrade thermochemical sorption system using sorption working pair $CaCl_2$-NH_3.

3.1.2. Absorption

As mentioned in adsorption section, those systems can be classified as open or closed. In absorption processes, only closed systems are found and are comparable with closed adsorption systems in the sense of presenting two essential components being the condenser and the evaporator. In the case of the reactor the main differences appear. While a generator and absorber are in absorption technologies, an adsorber and desorber are the core of the adsorption technologies. This is exemplified in Figure 20.

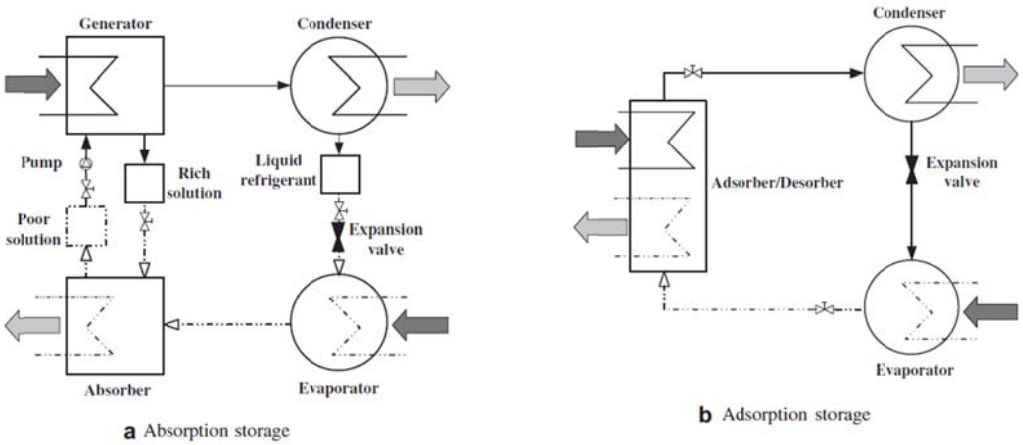


Figure 20. Comparison schemes between (a) absorption and (b) adsorption closed systems [3]

Moreover, and as shown in Figure 21, within the closed absorption technologies, single-stage or double-stage have been designed for sodium hydroxide and water, $NaOH/H_2O$, as absorption pair [327,350]. In single-stage, during charging phase, solar heat is supplied to the low-concentration solution in the regenerator. The water vapour is desorbed, flows to the condenser where it condenses. The condensated water is collected inside the water storage tank. To discharge the NaOH storage, the stored water is evaporated in an evaporator using a low temperature source. The vapour is absorbed by the highly concentrated NaOH lye in the absorber and heat is released. The main advantage of NaOH is its cost in relation with its storage density. The energy storage density depends on the charging and discharging temperature and is between 170 and 400 kWh/m³. The process has been successfully demonstrated in a prototype plant with a capacity of 200 l of sodium hydroxide [338].

A double-stage system (Figure 21 right) was designed to improve the heat production temperature level during discharging process or to reduce the required temperature level during charging process. The overall working principle is similar to the common system (single-stage process) except for an added regenerator 2, condenser 2 and heat exchanger. To regenerate the storage, the NaOH solution flows from regenerator 1 and is split up into two flows: the first part enters condenser 2 and the second part enters regenerator 2. The condenser 2 is working as an absorber, which absorbs the vapour desorbed in regenerator 2. The intermediate concentration solution that leaves condenser 2 returns to regenerator 1. As the pressure in regenerator 2 is almost the same in condenser 2, which is lower than that in regenerator 1, the concentration of the solution can be increased at lower temperature level (95 ºC) than that required in regenerator 1 to reach the same concentration (150 ºC). The main drawbacks of double-stage processes are the decrease in storage density and the complexity of the system, which needs more tanks and heat exchangers [327].

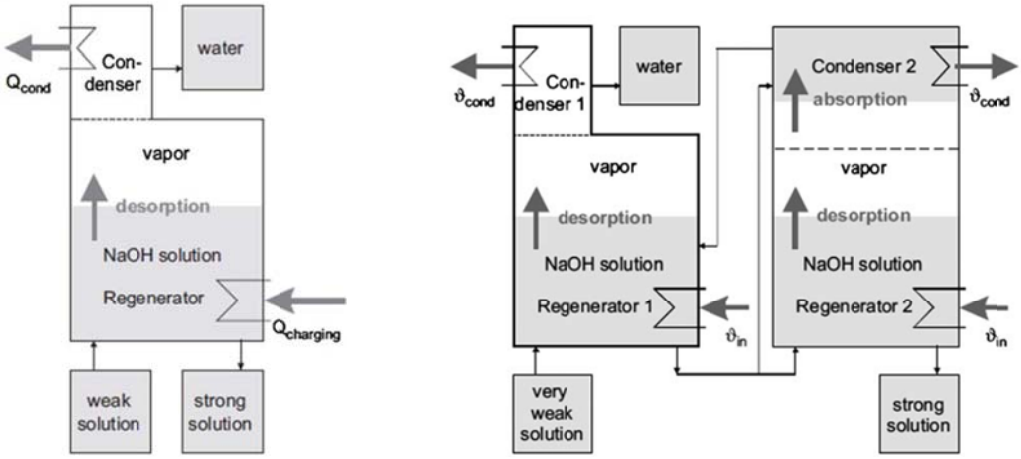


Figure 21. Operating principle (charging) of closed absorption storage technology, left: one stage, right: double-stage [350].

The system based on lithium chloride, LiCl, can deliver either cooling (cooling mode) or heating (heating mode). Crystallization, a long time bottleneck point, has been overcome and that enables the enhancement of the storage density and the COP with a so-called ‘‘closed three phase absorption’’ (LiCl solution, salt crystals and water) [351]. The storage density experimentally reached is 253 kWh/m^3 of LiCl salt. However, the high price of LiCl led the authors to dismiss prospect of long-term storage, as said before. For charging, poor solution is pumped over the heat exchanger and comes closer and closer to the saturation point so that solid crystals are formed and collected in the vessel, as they fell under gravity. A sieve prevents them from following the solution into the pump. The water vapour, which is desorbed, flows into the condenser by the gas pipe. The process is reversed during discharging, where the solution becomes unsaturated on the heat exchanger by absorbing the water vapour produced in the condenser (which becomes the evaporator). The poor solution falls into the vessel where it becomes saturated because of the dissolution of some crystals. The heat of evaporation is provided either by the building (cooling mode) or by the environment (heating mode). The heat of condensation and binding energy release is transferred to the environment (cooling mode) or to the building (heating mode) [327].

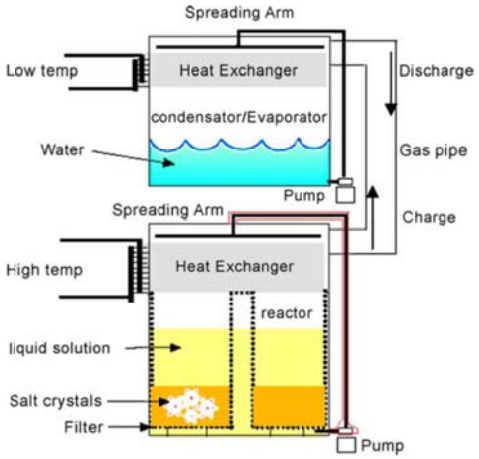


Figure 22. Absorption system based on LiCl [351]

Aqueous calcium chloride was investigated as long-term solar storage medium. The absorption system consist on a closed concept with just one vessel for both, concentrated and diluted solution of aqueous calcium chloride ($CaCl_2$). The closed storage concept combines absorption and sensible heat storage and achieves an energy density of approximately 105 kWh/m³ [352]. An experimental prototype with a 1500 l store has been set up and it could be demonstrated that the mixing rate of concentrated and diluted solution is very small [338].

Another absorption setup was designed on the basis of sulphuric acid and water [353]. In Figure 23 the scheme of the system can be observed. Two liquids were mixed in two different systems of multistage mixing column, and an application of heat of dilution to multipurpose energy utilization was analysed. The utility of heat of dilution is explained from the results of thermal characteristics of each system [353].

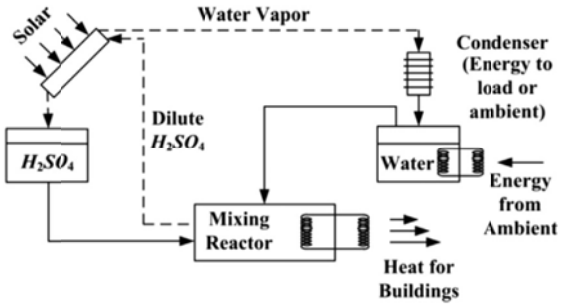


Figure 23. Absorption heat storage for sulphuric acid concentration difference [348,354]

Table 12. Sorption technologies along with its application and main features

		Institution/Project/Prototype name (years)	Application	Boundary conditions	Material confinement	Storage capacity	Energy density (prototype)	Power output/Discharge rate	COP	Open/Closed	Loss from theoretical	Cost	Ref
Physisorption	Zeolites 13X/H_2O	ZAE Bayern	Building. Buffer in district heating network	$T_{charging}$: 130ºC $T_{discharging}$: 65 ºC $T_{discharging(cold)}$: 11ºC	Bulk	1300 kWh 1751 kWh (cold)	124 kWh/m^3 for heating and 100 kWh/m3 for cooling [327] 124 kWh/m3 (heating, material) and 168 kWh/m3 (cold, material) [6]	135 kW	0.9 for heating 0.86 for cooling	Open	n.a.	n.a.	[6, 327]
		SPF	Buildings	$T_{charging}$:180 ºC $T_{dicharging}$: 55 ºC	n.a.	1 kWh	57.8 kWh/m3	0.8-1.8 kW	n.a.	Closed	Energy density of material (ratio to water 25/85 ºC) 180 kWh/m3	2-3000 €/m3	[6,327]
		SJTU	n.a.	$T_{charging}$: 350 ºC $T_{discharging}$: 15ºC	n.a.	5.5 kWh (cold)	167 kWh/m3 (material)	4.1 kW (cold)	n.a.	Closed	n.a.	n.a.	[6]
	Zeolites 4A/H_2O	Monosorp (2005-2007)	Buildings	$T_{charging}$: 180ºC $T_{discharging}$: 35 ºC	Extruded zeolites honeycomb structures	12 kWh	120 kWh/m3	1.0-1.5 kW	n.a.	Open	160 kWh/m3 (material)	2500-3500 €/m3	[6,327]

	Silica gel/H_2O	Hydes	Building. Heating and DHW	$T_{charging}$: 88 ºC	n.a.	n.a.	120 kWh/m3 of silica gel	n.a.	n.a.	Closed	20 %	n.a.	[327]
		Modestore	Building. Heating single-family house	$T_{discharging}$: 88 ºC	n.a.	13 kWh	33.3 kWh/m3	0.5- 1.0 kW	n.a.	Closed	Energy density of material (ratio to water 25/85 ºC) 50 kWh/m3	4300 €/m3	[6,327]
Chemisorption	$MgCl_2/H_2O$	ECN (2013)	Heating	$T_{discharging}$: 64 ºC	bulk	2.4 kWh	139 kWh/m3 (material) [6] 0.5 GJ/m3 [329]	0.15 kW	n.a.	Closed	n.a.	n.a.	[6,329]
	$MgSO_4 \cdot 7 H_2O$	ECN	Buildings	150 ºC	n.a.	n.a.	420 kWh/m3	n.a.	n.a.	Closed	n.a.	4870 €/m3	[327]
	Na_2S/H_2O + cellulose	ECN	n.a.	$T_{discharging}$: 5-20 ºC	n.a.	3.2 kWh 2.1 kWh (cold)	1070 Wh/kg (material) 700 Wh/kg (material, cold)	0.5-0.7 kW	n.a.	Closed	n.a.	n.a.	[6]
	Na2S+graphite/H2O	Chiang Ma University	Buildings	$T_{charging}$: 80-95 ºC	n.a.	0.56 kWh	2240 Wh/g (material)	0.15-0.24 kW	n.a.	Closed	n.a.	n.a.	[6]
	SrBr2+Expanded graphite/H2O	PROMES 2008	Heating and cooling	$T_{charging}$: 80 ºC	n.a.	60 kWh for heating 40 kWh for cooling	n.a.	2.5-4.0 kW	n.a.	Closed	n.a.	n.a.	[6,329]
	BaCl2 + expanded graphite/ammonia	PROMES 2012	Solar air conditioning	$T_{charging}$: 60-70 ºC $T_{discharging}$: 4 ºC	tubes	20 kWh (cold)	114 Wh/kg (cold)	5 kW (cold)	n.a.	Closed	n.a.	n.a.	[6,329]

Physisoprtion+ chemisorption	Zeolites 13X + 15% $MgSO_4/H_2O$	SolsSpaces (2012-2014)	n.a.	n.a.	packed bed of zeolite spheres	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[338]
	Zeolites + salt	CWS-NT-concept	n.a.	$T_{charging}$: 130 ºC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[6]
	Attalpugite+ 30 % $CaCl_2/H_2O$	Fraunhofer IGb, SeoSys GmbH 2012	Heating	n.a.	n.a.	200 Wh/kg	n.a.	n.a.	n.a.	Open	Scaling effects observed	n.a.	[329]
Absorption	NaOH Two phase	EMPA	Buildings	$T_{charging}$: 93 ºC $T_{discharging}$: 70 ºC	n.a.	8.9 kWh	5 kWh/m3	1 kW	n.a.	Closed	Energy density of material (ratio to water 25/85 ºC) 250 kWh/m3	250 €/m3	[6,327]
	LiBr/H2O	n.a.	Air conditioning	n.a.	Dilute solution volume, concentrated solution and water volume	58.2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[3]
		n.a.	Air conditioning	n.a.	Mixed storage volume and water volume	116.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	[3]

		LOCIE-CNRS	n.a.	$T_{charging}$: 75-90 ºC $T_{discharging}$: 30-40 ºC	n.a.	13 kWh	n.a.	n.a.	n.a.	Closed	n.a.	n.a.	[6]
	LiCl Three phase	TCA, SERC	Buildings	85ºC 25 ºC	n.a.	35 kWh	85 kWh/m3	8 kW	n.a.	Closed	Energy density of material (ratio to water 25/85 ºC) 253 kWh/m3	3600 €/m3 material	[6,327]
	$CaCl_2/H_2O$	University of Minesota, USA 2012	n.a.	$T_{charging}$: 138 ºC	n.a.	n.a.	381 kWh/m3 (material)	n.a.	n.a.	Closed	n.a.	n.a.	[6]
	NH_3/H_2O	Delft University 1987		$T_{charging}$: 93 ºC $T_{discharging}$: 43 ºC	n.a.	40 kWh	119 kWh/m3 (material)	n.a.	n.a.	Closed	n.a.	n.a.	[6]

3.2. Materials

Sorption storage materials are usually classified as the technologies, absorption and adsorption, where one can find physisorption and chemisorption. Then, mixtures between these last two, physisorption and chemisorption, are being developed and tested and thus are referred as composites. Composites can also include mixtures of any sorption material with another inert material such as graphite, cellulose, etc. In Figure 24 a possible classification is given, where sorption materials are divided in four groups. Chemical reactions group can also be known as chemisorption materials and more in a wider concept as thermochemical materials. Thermochemical materials also encompass chemical reactions without sorption, such as redox reactions for high temperature thermal energy storage [355], which is out of the scope of the present review. Some of the sorption storage materials are also implemented in sorption technologies without storage, under different conditions. More fundamental information regarding sorption materials and its properties in a non-storage technology can be found in section 2.2.

The most chracterized sorption storage materials are listed in Table 13 along with its main properties under given boundary conditions. All the sorption materials listed there make pair with water, as vapour in the case of adsorption and in liquid phase in the case of absorption.

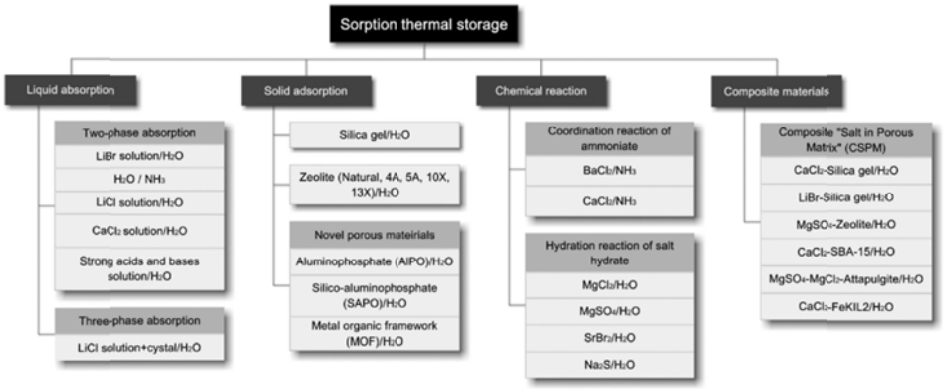


Figure 24. Possible classification of sorption thermal energy storage materials [6]

3.2.1. Sorption material properties

Regarding sorption storage materials, main properties requirements are [356]:

- High energy density: to store the maximum energy in the minimum volume.
- Reaction temperature reachable by a solar collector (below 150 ºC): the heat source to proceed with the endothermic reaction is the sun.

- Non-toxicity and non-flammability: since will be implemented in buildings and need to accomplish health and safety conditions.
- Non-corrosiveness: especially with the reactor material in contact.
- Stable after several hydration/dehydration reactions: to ensure long term performance of the system.
- Low cost: to be market competitive.

When choosing a sorption material one of the properties that are the first to look at is the energy density given at certain operating conditions, charging/discharging temperature, evaporator/condenser temperature, for closed systems, and ambient temperature. To see how operating conditions are influencing storage capacity Figure 25 is depicted. The first is wanted to be as high as possible in order to store the maximum amount of energy in the lowest volume. Energy densities, under given conditions, and properties of the most common sorption materials are gathered in Table 13.

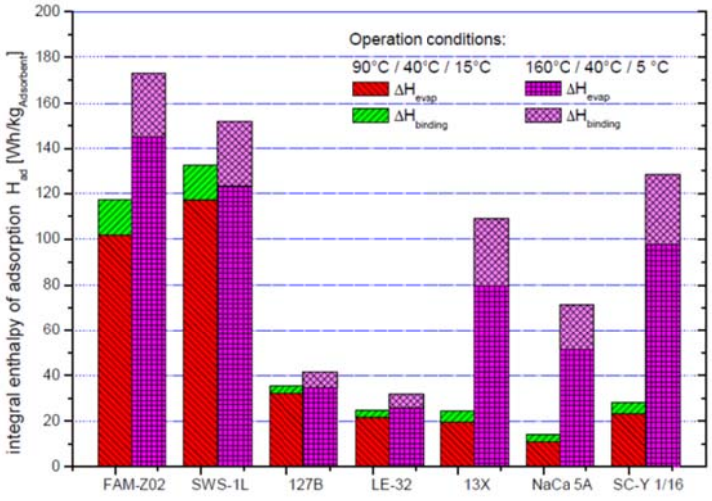


Figure 25. Integral enthalpy od adsorption of different sorption materials under different operating conditions [357]

Another key parameter is the durability and stability that should be examined under repetitive cycles to demonstrate their operability. With an increasing number of thermochemical cycles, a sorption material degrades and its behaviour may change. The stored heat and the overall efficiency of the storage system may decrease over time and numbers of cycles. Also corrosion is one of the drawbacks that sorption materials present and needs to be addressed, especially when working with salt hydrates (chemisorption) and absorption, and being the vessel materials of the containers, heat exchangers, and reactors, metals [357,359].

One of the major issues to be overcome in thermochemical energy storage and sorption is the low heat and mass transfer. Then, directly related to heat and mass transfer regarding the sorption materials itself, thermal conductivity and permeability are key parameters for adsorption beds [360,361]. Nevertheless, reactors design should play an important role when enhancing heat and mass transfer [329].

3.2.2. Physisorption

a. Zeolites/H_2O

Zeolites are alumina silicates with high microporosity. There are synthetic and natural zeolites. A study was conducted comparing natural zeolites and synthetic zeolite 13X and it was concluded that natural zeolites could be used as a storage material instead of the 13X synthetic zeolite when the heating temperature is below 100 ºC [362]. For the zeolite/H_2O pair, the adsorption heat is about 3300-4200 kJ/kg, higher than that of silica gel/H_2O pair [22]. Additionally, the temperature of desorption can reach high than 200 ºC, at which point the zeolite/H_2O can be still stable. Zeolites can be employed for different applications as shown in Table 12. Different kinds of crystal cell units of zeolite are shown in Figure 9. The volume of pores for type X and Y zeolites, whose void ratio can be as high as 50% when there is no water adsorbed, is larger than that of other types of pores.

There are other kind of adsorbents sometimes also referred as zeo-like materials because their crystalline structure is somehow similar to the classical zeolites. The two classes that show the most promising features are the aluminophosphates (AlPOs) and the silico-aluminophosphates (SAPOs) [357]. Moreover, MOFS are also being studied and have been mentioned in section 2.2.2 in this review.

b. Silica gel/H_2O

The storage density of silica gel is up to four times that of water, being around 2500 kJ/kg and the desorption temperature can be very low, but above 50 ºC [3]. Desorption temperature should not be higher than 120 ºC, and it is usually below 90 ºC. Approximately 4-6 wt.% water is connected with a single hydroxyl group on the surface of a silica atom to maintain the adsorption capacity. If the desorption temperature is too high (above 120 ºC), adsorption performance will drop significantly, even to the point of losing its adsorption capacity. In addition, the adsorption quantity of this pair is low, about 0.2 kg/ kg. Silica gel is commercially

available as pellets or beads of quite spherical shape in diameter from 1 to 4 mm [361]. Theoretical analysis of a closed adsorption process in a granular silica gel bed through simulations has been published [363] and is concluded that the adsorption time decreases with the particle size until a size range where the value adsorption time is practically constant (in this case, grain sizes in the order of magnitude of 0.1 mm. The minimum adsorption time could then be obtained in this range: optimum diameter of 0.2 mm and 0.6 mm for bed thickness of 10 mm and 40 mm, respectively. Beyond this range, the adsorption time quickly increases with the particle size. This behavior is justified by the change in the limiting adsorption step [361,363].

3.2.3. Chemisorption

a. Salt hydrates

A quite recent review shows an exhaustive screening between 125 salt hydrates to be used as sorption storage material. The results show that for an application that requires a discharging temperature above 60 ºC, $SrBr_2 \cdot 6H_2O$ and $LaCl_3 \cdot 7H_2O$ appear to be the most promising, only from thermodynamic point of view. However, the maximum net energy storage density including the water in the water storage tank that they offer (respectively 133 kWh/m^3 and 89 kWh/m^3) for a classical thermochemical heat storage process are not attractive for the intended application. Furthermore, the thermal efficiency that would result from the storage process based on salt hydrates without condensation heat recovery appears also to be very low (lower than 40% and typically 25%) [364].

Four promising salt hydrates: $MgSO_4$, $MgCl_2$, $CaCl_2$, and $Al_2(SO_4)_3$ were proposed for seasonal heat storage of solar energy in the built environment and tested under practical conditions at 150ºC/10-50ºC/10ºC [365], where 150 ºC was the assumed maximum temperature that can be delivered by a medium temperature collector (vacuum tube) during the summer period and 10 ºC was the assumed temperature of the borehole heat exchanger connected to the evaporator/condenser. The performance of the material was assessed by measuring the temperature lift of the bed during the sorption process. The $MgCl_2$ reached a maximum temperature lift of 19 ºC while the $CaCl_2$, the $MgSO_4$, and the $Al_2(SO_4)_3$ reached a maximum temperature lift of 11 ºC, 4 ºC and 1 ºC, respectively. However, the $MgCl_2$ and $CaCl_2$ tend to form a gel-like material during the sorption process due to their hydroscopic nature [341].

The hydration experiments have shown that for both, magnesium and copper sulphate monohydrate, a high water vapour pressure is needed for a sufficiently high reaction rate. The

reaction of copper sulphate monohydrate with humid air is limited by the equilibrium to a maximum operating temperature of 60 °C. Although higher temperature lifts and operating temperature were observed using MgSO4, this is not directly correlated with a faster reaction rate. To determine the reaction rate, further research has to be done in micro- and macro-scale to understand the reaction kinetics and mass transfer processes, especially with respect to the different hydrates of magnesium sulphate [366]. Moreover, mixtures of abovementioned salts are being studied at lab scale [367].

b. Composites

In this section, referred as composites, salt hydrates mixed with additives and combination of physic and chemisorption materials are considered. The mixing of an additive can be done in the sense of enhancing the overall material effective conductivity and thus improve heat transfer, enhance mass transfer by providing higher permeability or to prevent some sorption material drawback which have been experimentally detected such as agglomeration, melting, slow kinetics, etc.

Usually hygroscopic salts present high energy storage density. However, a very slow reaction rate associated with a very low temperature lift in the reactor was observed during the experiments performed. A way to enhance the reaction rate and thus the heat release is to use a physisorption material which might consist on a combination of an active (e.g. zeolite) or a passive (e.g. ceramics), porous, supporting material and salt. The supporting material primarily defines the structure, consistency and form of the storage material. The salt enhances (in the case of an active carrier structure) or defines (in the case of a passive carrier structure) the energy storage capacity of the material [91].

A way to enhance poor heat transfer is to add a high conductive material, such as graphite is by far the most selected additive when developing TCM composites with the purpose of enhancing TCM thermal conductivity. When comparing different host matrices or/and additives, graphite presents the highest conductivity values [333]. For instance, Mauran et al. [368] reported thermal conductivities of about 10-40 W/m·K for $CaCl_2$-expanded natural graphite. Furthermore, expanded graphite prevents agglomeration and raises heat transfer [369]. Composite graphite based TCM are being tested at lab and reactor scale.

Despite the high theoretical energy density of $MgSO_4 \cdot 7H_2O$ (dense salt: 780 kWh/m^3), the rate of the reaction and the power delivered is not sufficient for practical use. Therefore, the material needs to be dispersed over a larger exchange surface to react at suitable rate and to release

greater thermal power. Obviously, this decreases the storage density. Various porous matrixes to disperse this salt in with the aim to optimise the heat transfer or the power density of $MgSO_4 \cdot 7H_2O$, while preserving the energy density as high as possible, were tested [370]. Composite materials made of magnesium sulphate and sorption materials, such as zeolites and silica gels, were prepared in such a way that the porosity of the sorption materials is preserved. The water vapour can therefore react which both the salt and the matrix. These composite materials are designed with 50% of the theoretical energy density of the dense salt. The results show that zeolite/$MgSO_4$ composite is more satisfactory than the others. Indeed, temperature lifts around 30 ºC and maximal power of 28 mW/g have been obtained during the hydration of the zeolite/MgSO4 composite.

The $CaCl_2$-silica gel composite has also been extensively studied, the composite containing a 30 wt.% $CaCl_2$ solution showing a storage capacity of 283 Wh/kg at the relatively low charging temperature of about 90 ºC [6]. Also, a new composite sorbent $LiNO_3$/vermiculite (SWS-9V), was specifically developed to operate at low regeneration temperature (<65-70 ºC), and demonstrated a remarkable heat storage capacity of 250 Wh/kg [6].

c. Ammoniated salts

A solid-gas reaction of ammonium thiocyanate (NH_4SCN) and ammonia produces liquid ammoniate ($NH_4SCN \cdot n NH_3$). This system offers a medium for thermal energy storage or a chemical heat pump system [348,371]. Other interesting sorption ammoniated salts are gathered in Figure 26a.

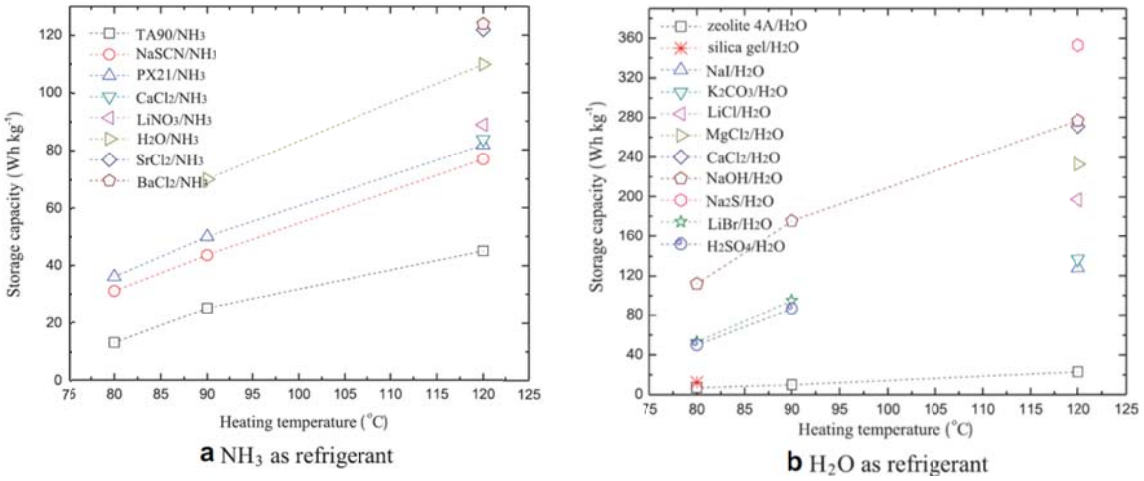


Figure 26. Storage capacity of different sorption working pairs with ambient temperature of 35 ºC and evaporation temperature of 5 ºC [3,372]

Thermal properties of working pairs for air conditioning and subzero applications were extracted and summarized as shown in Figure 26 [372]. The summary examines them under the same conditions of an ambient temperature of 35 ºC and evaporation temperature of 5 ºC. From the figures above, the most suitable and efficient working pair for the sorption storage system is water and solid/gas reaction used as the refrigerant and sorbent, respectively [3,373].

3.2.4. Absorption

The most characterized absorption pairs are listed in Table 13 along with its main properties under given boundary conditions. Among these ones, $NaOH/H_2O$, $LiBr/H_2O$, $LiCl/H_2O$, and $CaCl_2/H_2O$ are the most studied pairs.

The energy density of $NaOH/H_2O$ as sorption storage material could be up to 900 MJ/m^3 of solution. A low level heat input at 150 ºC was needed to completely charge the system. Analyses show that the concentration ratio of the salt, the corresponding vapor pressure, and the temperature of the discharge are significant parameters. The heat storage capacity of the system is limited by a high temperature needed during the discharge phase [375].

$LiBr/H_2O$ is being implemented in single-effect absorption machines which are suitable for solar cooling applications due to good performance at the temperature available from conventional collectors [6]. Static simulations made based on an evaporation temperature of 5–10 ºC to produce heat at 25–33 ºC in winter, show storage density between 180 and 310 kWh/m^3 diluted solution [327]. A cascade absorption system with aqueous LiBr thermal energy storage and R-123 chiller in series were tested. A storage density of 90.9 kWh/m^3 was obtained while the volume was based on the volume of a mass concentration of 59% LiBr solution [6].

Metal chloride solutions developed for liquid absorption thermal storage mainly include LiCl and $CaCl_2$, which have been widely applied in open desiccant dehumidification and storage systems [6]. Based on the results presented by ClimateWell (in Sweden) this pair is not suitable for seasonal storage, not because of its storage density (253 kWh/m^3 LiCl salt), which is 2.7 times higher than that of water (25/85 ºC), but because of the high cost of the salt (3600 €/m3) [327] (see Table 12).

Table 13. Sorption storage materials along with its main properties under given boundary conditions

Sorption process classification		Sorption material	Boundary conditions	Water uptake/enthalpy reaction	Theoretical energy storage density (GJ/m^3)	Thermal conductivity (W/m K)	Density (kg/m^3)
Adsorption	Physisorption	Zeolites 4A	$T_{charging}$: 130 ºC, $T_{discharging}$: 65 ºC [329]	n.a.	0.58 (experimental) [329]	Solid grain: 0.18-0.4 [334] Granular bed: 0.03-0.15 [334]	n.a.
			$T_{charging}$: 180 ºC [6]		0.45 [6]		700 [6]
			$T_{charging}$: 150 ºC [6]		0.353 [6]		700 [6]
		Zeolites 13X	$T_{charging}$: 180 ºC [6] $T_{charging}$: 130 ºC, T_{cond}: 40 ºC [6] $T_{discharging}$: 65 ºC, T_{evap}: 5 ºC [6]		0.396 [6] 0.349 [6]		739 [6] 896 [6]
		Zeolite MgNaX	$T_{charging}$: 180 ºC [6]		0.461 [6]		732 [6]
		Zeolite LiX			0.576 [6]		711 [6]
		Zeolite CaNaA-60			0.418 [6]		671 [6]
		Zeolite NaCa 5A	$T_{charging}$: 130 ºC, T_{cond}: 40 ºC [6] $T_{discharging}$: 65 ºC, T_{evap}: 5 ºC [6]		0.205 [6]		801 [6]
		Zeolite Y			128 Wh/kg [6]		n.a.

		Microporus silica gel SG-127B	$T_{charging}$: 90 ºC, T_{cond}: 40 ºC [6] $T_{discharging}$: 40 ºC, T_{evap}: 15 ºC [6]	n.a.	0.09 [6]	Solid grain: 0.37-0.8 [334] Granular bed: 0.05-0.20 [334]	710 [6]
		Macroporus silica gel SG-LE32			0.054 [6]		620 [6]
	Chemisorption	$CaCl_2 \cdot 2H_2O/CaCl_2$	95 ºC	n.a.	1.1 [329]	Granular bed: 0.1-0.2 [334]	n.a.
		$CaCl_2 \cdot 2H_2O/CaCl_2$	$T_{discharging}$: 174 ºC [329] $T_{charging}$: 95 ºC [329] $T_{discharging}$: 35 ºC [329]	n.a.	0.60 [329] 0.72 [329]	n.a.	n.a.
		$Al_2(SO4)_3 \cdot 6H_2O$/ $Al_2(SO4)_3$	150 ºC [329]	n.a.	1.9 [329]	n.a.	n.a.
		$MgSO_4 \cdot 7H_2O/MgSO_4$	Turnover temperature: 122 ºC [334]	n.a.	2.8 [334] 1.5 [329]	n.a.	n.a.
		$MgSO_4 \cdot 7H_2O/MgSO_4 \cdot$ H2O	$T_{charging}$: 150 ºC [329] $T_{discharging}$: 105 ºC [329]	n.a.	2.3 [329]	n.a.	n.a.
		$MgSO_4 \cdot 7H_2O/MgSO_4 \cdot 0.1H_2O$	$T_{charging}$: 150 ºC [6]	n.a.	3.33 [6]	n.a.	1330 [6]
		$MgSO_4 \cdot 6H_2O/MgSO_4 \cdot$	$T_{charging}$: 72 ºC [329]	n.a.	2.37 [329]	n.a.	n.a.

		H_2O			1.83 (experimental) [329]		
		$CaSO_4 \cdot 2H_2O/CaSO_4$	Turnover temperature: 89 ºC [334]	n.a.	1.4 [334]	n.a.	n.a.
		$MgCl_2 \cdot 6H_2O/MgCl_2 \cdot H_2O$	$T_{charging}$: 150 ºC [329] $T_{discharging}$: 50-30 ºC [329]	n.a.	2.5 [329] 0.71 (experimental) [329]	n.a.	n.a.
		$MgCl_2 \cdot 4H_2O/MgCl_2 \cdot 2H_2O$	$T_{charging}$: 118 ºC [329]	n.a.	1.27 [329] 1.10 (experimental) [329]	n.a.	n.a.
		$MgCl_2 \cdot 6H_2O/MgCl_2 \cdot 2H_2O$	$T_{charging}$: 130 ºC [6]	n.a.	2.00 [6]	n.a.	1165 [6]
		$Na_2S \cdot 5H_2O/Na_2S \cdot 1/2H_2O$	$T_{charging}$: 80 ºC [6,329] $T_{discharging}$: 65 ºC [329]	n.a.	2.7 [329] 3.56 [6]	n.a.	928 [6]
		$SrBr_2 \cdot 6H_2O/SrBr_2 \cdot H_2O$	$T_{discharging}$: 23.5 ºC [329]	n.a.	2.3 [329] 2.08 (experimental [329]	n.a.	n.a.
		$Li_2SO_4 \cdot H_2O/LiSO_4$	$T_{charging}$: 103 ºC [329]	n.a.	0.92 [329]	n.a.	n.a.

					0.80 (experimental [329]		
		$CuSO_4 \cdot 5H_2O/CuSO_4 \cdot H_2O$	$T_{charging}$: 92 ºC [329]	n.a.	2.07 [329] 1.85 (experimental [329]	n.a.	n.a.
	Composites: Inert additives	$SrBr_2 \cdot 6H_2O/SrBr_2 \cdot H_2O$ + ENG	$T_{charging}$: 80 ºC [6]		0.63 [6]		1165 [6]
		$CaCl_2$ + ENGP-S-1	From 100 to 200 ºC	n.a.	n.a.	1.64 [374]	85 [374]
		$CaCl_2$ + ENGP-S-1		n.a.	n.a.	0.74 [374]	46 [374]
		$CaCl_2$ + ACF VI		Dehydration: 0.10 g/g, 235 J/g Hydration: 0.12 g/g, 198 J/g	n.a.	1.03 [374]	649 [374]
	Composites: Physisorption +	Aluminosilicate + 30 % $CaCl_2$	$T_{charging}$: 180 ºC [6]	n.a.	0.62 [6]	n.a.	972 [6]
		Mesoporous silica gel +	$T_{charging}$: 90 ºC, T_{cond}: 40 ºC [6]	n.a.	0.31 [6]	n.a.	646 [6]

	Chemisorption	33.7 % $CaCl_2$	$T_{discharging}$: 40 ºC, T_{evap}: 15 ºC [6]				
		Zeolite 13X + 15% MgSO4	$T_{charging}$: 150 ºC [6] $T_{discharging}$: 30 ºC [6]	n.a.	0.60 [6]	n.a.	922 [6]
		Zeolite 4A + 10% MgSO4	$T_{charging}$: 180 ºC [6]	n.a.	0.64 [6]	n.a.	797 [6]
		Bentonite + 40%$CaCl_2$	$T_{charging}$: 150 ºC [6]	n.a.	0.49 [6]	n.a.	695 [6]
		Attapulgite + $MgSO_4$ and $MgCl_2$ (mass ratio 20/80)	$T_{charging}$: 130 ºC [6] $T_{discharging}$: 30 ºC [6] 85 % RH	n.a.	442 Wh/kg [6]	n.a.	n.a.
Absorption		$LiBr/H_2O$	Without crystallisation $T_{heat\ driving}$: 74 ºC [3] With crystallisation $T_{heat\ driving}$: 93 ºC [3] $T_{charging}$: 72 ºC [6]	Without crystallisation 1535 kJ/kg [3] With crystallisation 2068 kJ/kg [3]	1.13 [6]	n.a.	557 [6]
		$LiCl/H_2O$	Without crystallisation $T_{heat\ driving}$: 68 ºC [3] With crystallisation $T_{heat\ driving}$: 78 ºC [3] $T_{charging}$: 65.6 ºC [6]	Without crystallisation 2922 kJ/kg [3] With crystallisation 5271 kJ/kg [3]	1.44 [6]	n.a.	328 [6]
		$NaOH/H_2O$	Without crystallisation $T_{heat\ driving}$:	Without	0.55 [6]	n.a.	355 [6]

		84 ºC [3] With crystallisation $T_{heat\ driving}$: 135 ºC[3] $T_{charging}$: 50 ºC [6]	crystallisation 3442 kJ/kg [3] With crystallisation 5225 kJ/kg [3]			
	$CaCl_2/H_2O$	Without crystallisation $T_{heat\ driving}$: 50 ºC [3] With crystallisation $T_{heat\ driving}$: 56 ºC [3] $T_{charging}$: 44.8 ºC [6]	Without crystallisation 628 kJ/kg [3] With crystallisation 1103 kJ/kg [3]	0.43 [6]	n.a.	469 [6]
	KOH/H_2O	$T_{charging}$: 63 ºC [6]	n.a.	1.13 [6]	n.a.	430 [6]

4. Conclusions

Sorption has advanced very much due to the immense amount of research carried out around heat pumping and solar refrigeration. Moreover, sorption and thermochemical heat storage attracted considerable attention recently since this technology offers various opportunities in the design of renewable and sustainable energy systems. This paper presents an extensive review of the state of the art of this technology, sorption, both for refrigeration and cooling and for storage, being the first time that both applications are presented together.

The operation principle of the technology is presented and the materials used or in research are listed and compared. The review shots that heat and mass transfer remains currently the main limitations. Mass and heat transfer challenges are common problematic in adsorption, chemical heat pumps and chillers as well as in thermochemical energy storage.

Given that the applications are in different states of development, also today's research is focussed in different aspects. Therefore, absorption heat pumping and refrigeration is today more focussed in the decrease of unit costs and increase of energy efficiency, adsorption is focussed in finding more efficient working pairs, and storage is testing the first prototypes and designing new ones minimizing energy losses throughout all the components, from the storage material to the final consumer

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